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May 19, 2008

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Subject: Quanta Resources Superfund Site Operable Unit 1 (OU1) Edgewater, New Jersey  
Administrative Order on Consent (AOC) II-CERCLA-2003-2012  
Remedial Investigation/ Feasibility Study Work Plan Addendum No. 4 for a  
Supplemental Remedial Investigation

Dear Mr. Ho:

In support of the Remedial Investigation/ Feasibility Study (RI/FS) activities at the Quanta Resources Superfund Site, Operable Unit 1 (OU1), CH2M HILL has prepared this letter Work Plan for a Supplemental Remedial Investigation (SRI), on behalf the AOC Respondents.

The work proposed herein is designed to address previously communicated data gaps in the area west of River Road (properties located at Block 93 as defined on Sheet 9 of the Borough of Edgewater, Bergen County, New Jersey tax map, herein referred to as Block 93 North, Central, and South), Block 94 (west of Old River Road), and the northwestern portion of the former Lever Brothers property. Furthermore, additional work components have been included in order to address select comments on the Draft RI Report (CH2M HILL, 2007a) from the United States Environmental Protection Agency (USEPA) and the New Jersey Department of Environmental Protection (NJDEP) (herein referred to collectively as the "Agencies"), that highlight uncertainty or data gaps that require additional investigation activities.

The preparation of a Final RI Report that addresses the remainder of Agency's comments on the Draft RI Report is currently underway. However, the data collection activities and subsequent evaluations that are required to address select Agency comments will not be completed in time for incorporation into the Final RI Report, and will instead be summarized in a Supplemental RI Report that will serve to update the applicable components of the Final RI, address the remaining Agency comments, and complete the RI process for the Site. It is the respondents' understanding and expectation that following

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completion of the field and reporting tasks outlined in this work plan addendum, the RI process for OU1 will be complete.

This document and serves as an addendum to the original RI/FS Work Plan (Parsons, 2005a). An update to the current QAPP as amended (CH2M HILL, 2005; 2006a) is included herein as Attachment A and includes the required information for proposed analyses not currently addressed in project specific documents. An addendum to the original RI/FS Field Sampling Plan (FSP) has also been prepared as part of this submittal and is included herein as Attachment B. Except as otherwise noted herein, the work described in this document will be conducted in accordance with the applicable methods and procedures outlined in detail in the original OU1 RI/FS Work Plan and relevant prior addendums.

## Setting and Background

### OU1

A detailed description of the Site background and physical setting is provided in the original RI/FS Work Plan (Parsons, 2005a). RI activities have been ongoing at OU1 since July 2005 and a Draft RI Report (CH2M HILL, 2007a) was submitted to the Agencies on November 15, 2007. Agency comments of the Draft RI Report were received on April 7, 2008.

A Scope of Work (SOW) outlining proposed additional soil and groundwater data collection in the area of Block 93 and the northwestern portion of the former Lever Brothers property (RI/FS Work Plan Addendum No. 2) (CH2M HILL, 2007b) was originally prepared and submitted to the Agencies on March 22, 2007. Subsequently, additional soil and groundwater data was collected as part of the *Characterization of Cinder/Ash and Reddish-Purple Soils* (CH2M HILL, 2007c) and the *Jono's Restaurant Building Vapor Intrusion Evaluation* (CH2M HILL, 2007d). These data were evaluated and incorporated into the Draft RI Report. In consideration of these additional data, as well as the evaluations presented in the Draft RI Report and the subsequent written comments received by the Agencies on April 7, 2008, the original March 22, 2007 Block 93 Work Plan and Field Sampling Plan Addendum has been modified. This RI/FS Work Plan Addendum and its attachments serve to update and replace that document.

### OU2

OU2 is located on a tidally influenced mud flat in the Hudson River to the east of OU1. These mud flats are exposed up to a distance of approximately 500 ft from shoreline during low tide, and are flooded under approximately 6.5 ft of water during high tide. The river sediments consist of silt to clayey silt. Non-aqueous phase liquid (NAPL) coal tar has been observed in near shore sediments at depths of up to 50 feet below the sediment surface, and oily sheens have been observed sporadically in the mud flats adjacent to the Quanta Resources property. Absorbent booms are maintained to control the sheens. A detailed

description of the Site background and physical setting is provided in the OU2 Preliminary Site Characterization Report (PSCR) (CH2M HILL, 2007e).

Operable Unit 2 (OU2) RI activities have been ongoing since October 2006, and a Draft PSCR was submitted to the Agencies in July 2007. The OU2 RI field investigation documented in the PSCR characterized the lateral and vertical distribution and extent of organic constituents and coal tar as well as arsenic in the sediment of OU2. In addition to potential impacts from groundwater discharge from OU1, pore water in OU2 may be affected by coal tar and other constituents in sediment. A scope of work for completing a Baseline Ecological Risk Assessment (BERA) for OU2 is currently being developed.

## Objectives the Supplemental Remedial Investigation

As with all investigations related to the OU1 RI/FS, the general objective of this work is to develop a dataset of sufficient quantity and quality to adequately assess the nature and extent of constituents at OU1 and to assess the potential risks posed by affected media in order to allow for the development of appropriate and effective mitigation/cleanup technologies.

Specific objectives of the SRI Work Plan have been developed and are presented below in context of the individual Agency comments that they are intended to address:

Objective	Draft RI Agency Comment(s) Addressed
1.) Determine the nature and extent of Site-related constituents and arsenic in the vicinity of Block 93 and the Northwest portion of the former Lever Brother's property and in the intersection of Gorge and River Roads.	GC#5, SC#'s 73, 97a
2.) Determine the nature and extent of non-aqueous phase liquid (NAPL) in the northeastern portion of the former Lever Brother's property (near MW-106A)	SC# 46
3.) Refine nature and extent of NAPL behind and at the flanks of the wooden bulkhead	SC#'s 83, 85, 104, BTAG# 6, 8
4.) Determine the dimensions of the wooden bulkhead to evaluate its role in limiting NAPL migration	SC#'s 83, 96a, 97a, BTAG# 6, 8
5.) Supplement existing data to sufficiently characterize risk to Human Health at Block 93 Central and South and for groundwater at the Site as a whole	GRAC #1
6.) Begin collection of data to confirm stability of organic constituents and arsenic in groundwater at OU1	SC# 39, 92c, ACC#7
7.) Confirm distribution and mobility of arsenic in groundwater within and downgradient of suspected source zones at OU1	SC#92b, 92d, 96c, 116a, ACC#1, 2, 3, 6,

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- 8.) Characterize groundwater flow paths and distribution and fate and transport of coal tar constituents (VOCs and PAHS) and arsenic across the groundwater/surface water (GW/SW) transition zone(s) between OU1 and OU2. GC#18, SC#'s 83, 85, 96a, 97a, 104, BTAG#9, 10

Notes:

GC- General Comment

SC- Specific Comment

ACC- Arsenic/Cinder Comment

BTAG-Biological Technical Assistance Group Comment

GRAC- General Risk Assessment Comment

In addition to the objectives outlined above, secondary objectives of the proposed work are to:

- Provide information for evaluating potential risks associated with coal tar constituents and arsenic within pore water at OU2
- Guide the collection of additional information on groundwater discharge if necessary for remedy design at OU2.

## Data Needs

To meet the objectives outlined above and complete the RI process for the site, data needs have been identified and are presented below relative to the types of questions they are intended to address.

### NAPL and Coal Tar Constituents in Soil

#### Block 93 North, Central and South and River Road (Objective #1)

- Soil screening, visual observations, and TarGOST® data for subsurface soils across Block 93 North, Central, and South, Block 94 and the northwest portion of the former Lever Brothers property to determine the lateral and vertical extent of two lenses of coal tar identified at 10 to 15 and 20 to 30 feet below ground surface (bgs) between the northeastern corner of Block 93 South and northwestern corner of the former Lever Brothers property.
- Soil screening, visual observations, and TarGOST® data for subsurface soils in order to confirm the southerly and westerly extents of NAPL observed at the top of the peat layer in the central portion of Block 93 North during the Cinder/Ash Investigation (soil borings SB-27 and SB-30).
- Soil screening and visual observations for subsurface soils in the southern portion of Block 92.01 (to the north of Gorge Road) and within the intersection of Gorge and River Roads to refine the lateral and vertical extent of NAPL in soil.



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- Analytical data for subsurface soils on Block 93 North, Central and South, Block 94, and within the intersection of Gorge Road and River Road to confirm TarGOST® and NAPL screening methods, evaluate the presence of solid tars, and quantify concentrations as well as the lateral and vertical extents of organic constituents in soil relative to screening criteria.
- Monitoring well installation and NAPL measurements within NAPL Zone 4 (NZ-4) to determine the mobility/recoverability of NAPL observed at Block 93 South during the fall 2006 Supplemental Investigation (location TL12-10.75).

**Former Aboveground Storage Tank in Northeast Corner of Former Lever Brothers Property (Objective #2)**

- Soil screening, visual observations, and TarGOST® data in the northeast corner of the former Lever Brothers property in the vicinity of a former aboveground storage tank (AST) of unknown contents to confirm the type of NAPL previously observed in soils at boring MW-106A, and whether it is coal tar.
- Analytical data for subsurface soils in the vicinity of MW-106A in order to confirm TarGOST® and NAPL screening methods, and determine if it is liquid coal tar or some other type of NAPL perhaps related to the former AST.

**Wooden Bulkhead/Shoreline Area (Agency Comments: Objective #s 3, 4 and 8)**

- Soil screening, visual observations in borings drilled directly behind and along the wooden bulkhead extending beyond the northern and southern limits of the bulkhead to confirm lateral and vertical distribution of NAPL present in this area.
- Completion of borings and installation of additional monitoring well along the shoreline at the former Celotex property to determine whether NAPL between NZ-2 and NZ-5 is contiguous and if NAPL in NZ-5 is mobile/recoverable.
- Surface geophysical survey work involving multi-frequency electromagnetic induction (EM), electrical resistivity (ER) and ground penetrating radar (GPR) and borehole survey work potentially involving downhole GPR and vertical seismic profiling (VSP) are proposed to evaluate the dimensions and characteristics of the known wooden bulkhead and possible landward bulkheads or former shoreline features. In addition, these data may help to further characterize the distribution of NAPL in the vicinity of the bulkhead.

**Arsenic in Soil**

- Visual observations and analytical data for metals in soil in the southern portion of Block 92.01 (to the north of Gorge Road) and within the intersection of Gorge Road and River Road to refine the lateral and vertical extent of pyritic material (reddish-purple soils) to the west of the former acid plant. (Objective #1)

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- Visual observations and analytical data for metals in soil across Block 93 North, Central and South, Block 94, and the intersections of Gorge Road and River Road and Gorge Road and Old River Road to further evaluate the source of detected arsenic. (Objective #1)

### **Organic Constituents and Arsenic in Groundwater**

- Groundwater analytical data for Block 93 Central and South, Block 94, and the intersection of Gorge Road and River Road in order to assess the extent of site-related constituents and metals in groundwater to the west of River Road. (Objective #1)
- Groundwater analytical data across multiple events for organic constituents and arsenic in select wells throughout OU1 for the purpose of understanding the current distribution of site-related constituents and confirming the stability of groundwater conditions over time. (Objective #6)
- Hydraulic head information for unconfined groundwater across and upgradient (west) of Block 93 North, Central, and South in order to confirm the direction of groundwater flow in these portions of the site. (Objective #1)
- Groundwater analytical data for key geochemical parameters across OU1 to support groundwater geochemistry and arsenic mobility evaluations within and downgradient of known source areas and across varying geochemical conditions at the Site. (Objective #7)
- An evaluation of the phases in which arsenic is present in soil within select arsenic source areas and along key potential groundwater flow transects of areas in order to determine the capacity and stability of arsenic attenuation through adsorption and confirm the role of iron oxyhydroxides in limiting arsenic mobility downgradient of source areas and prior to reaching OU2. (Objective #7)
- Groundwater analytical data for arsenic (III and V) speciation to confirm the speciation of arsenic in groundwater and to further assess arsenic fate and transport within and downgradient of known source areas and across varying geochemical conditions at the site (Objective #7).
- Geophysical data in the vicinity of the wooden bulkhead in order to determine the depth and breadth of the structure and its role in NAPL and groundwater migration from OU1 to OU2 (Objective #s 4 and 8)
- Hydraulic head information along the shoreline adjacent to, and to the north and south of the wooden bulkhead and at varying depths within OU1 and OU2 to determine groundwater flow paths from OU1 to OU2. (Objective #8)
- Identification of groundwater upwelling zones at OU2 downgradient of observed impacts in groundwater at OU1. (Objective #8)

- Analytical data for organic constituents and arsenic in shallow pore water and surface water at identified groundwater upwelling zones and in deeper pore water at varying depths within OU2. (Objective #8)
- Shallow pore water analytical data for arsenic (III and V) speciation within OU2 to confirm arsenic mobility and toxicity in the biologically active zone and immediately prior to discharge to OU2 surface water. (Objective #8)

### **Human Health Risk Assessment**

- Analytical data for subsurface soils between 0-2 feet bgs and 0-10 feet bgs across Block 93 Central and South in order to adequately characterize potential risks to human health at properties where site-related impacts have been observed to date. (Objective #5)
- Analytical data for shallow groundwater throughout Block 93 Central and South, in order to adequately characterize potential human health risk. (Objective #5)

The need for data to evaluate the fate and transport of site-related constituents and arsenic in groundwater will also serve to address data needs for OU2, and supplement the data to be collected as part of the RI and Baseline Ecological Risk Assessment (BERA) for OU2. Specifically, shallow pore water samples collected for arsenic speciation as part of this SOW will enable an evaluation of the risk to benthic receptors in the biologically active zone of the sediment where groundwater discharge is preferentially occurring. In addition, surface water sample results for organic constituents and arsenic will allow for the evaluation of the potential for risk to human health associated with direct contact to surface water at OU2. This work plan does not intend to outline the approaches to be taken in evaluating human health and ecological risks associated with OU2.

### **Scope of Work**

This section presents the tasks required to address the objectives and data needs described above. This SOW was prepared in accordance with 'Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA' (USEPA, 1988) as well in consultation of the following guidance documents:

- 'Using Dynamic Field Activities for On-Site Decision Making: A Guide for Project Managers' (USEPA, 2003)
- 'Monitored Natural Attenuation of Inorganic Contaminants in Groundwater, Volumes 1 and 2' (USEPA, 2007)
- 'The Impact of Groundwater/Surface Water Interactions on Contaminant Transport with Application to an Arsenic Contaminated Site' (USEPA, 2005).

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The field work and data collection components of this SOW have been broken into seven (7) main tasks as outlined below.

Task	Description
Task 1	TarGOST® Profiling
Task 2	Organic Constituents and Metals Soil Sampling
Task 3	Arsenic Solid Phase Association Sampling
Task 4	Monitoring Well Installations and Groundwater Grab Sampling
Task 5	2008 Semi-Annual Groundwater Sampling
Task 6	Shoreline and Wooden Bulkhead Characterization
Task 7	Groundwater/Surface Water Interaction (GSI) Evaluation

The components of each task of these tasks are discussed in detail in the following sections. Proposed investigation locations are illustrated in the attached Figures 1 through 7. Additional information about sampling depths, analytes and specific data quality objectives for each proposed location are provided in the attached Tables 1 through 7.

### **Task 1 - TarGOST® Profiling**

A dynamic "real-time" NAPL delineation program using TarGOST® coupled with direct-push drilling techniques has been designed as part of this RI/FS Work Plan Addendum, in order to further define the distribution of coal tar NAPL west and south of the Quanta property. This comprehensive determination of the distribution of free-phase or residual NAPL coal tar will allow for the proper accommodation of any risks associated with the presence of NAPL in these areas and a better understanding of the accessibility and recoverability of the NAPL, which will ensure the development of more appropriate and cost-effective mitigation/cleanup technologies as part of the Feasibility Study process.

The TarGOST® NAPL delineation program described herein uses technologies that are intended as screening tools. The intent of this program is not to generate additional analytical data for soil or groundwater, but rather to more fully characterize the location and extent of coal tar NAPL in subsurface soils. A large analytical dataset already exists for most of the Site that includes samples collected as part of the original RI/FS Work Plan

(Parsons, 2005a) and supplemental studies as well as historical data for both the Quanta property and adjacent properties. The collection of additional analytical soil samples are also proposed as part of this RI/FS Work Plan Addendum throughout the areas where TarGOST® will be implemented. Soil sampling will be performed as part of subsequent direct-push and rotasonic drilling programs described in the following sections. TarGOST® results will be used to identify impacted intervals for soil sampling. These samples will be used to confirm the effectiveness of the TarGOST® technology and supplement existing data sets in order to complete the delineation of Site-related constituents and quantify potential risks associated with current and future uses at properties within the extent of OU1. Proposed TarGOST® boring locations are illustrated in context of the current delineation of NAPL on Figure 1. Table 1 summarizes the specific data quality objectives for each proposed TarGOST® location.

- Up to twenty (20) TarGOST® borings will be advanced to a maximum depth of 30 feet bgs across Block 93 North, Central, South, and the northwestern portions of the former Lever Brothers property.
- Up to two (2) additional TarGOST® borings will be advanced to a maximum depth of 30 feet bgs in the northeast corner of the former Lever Brothers property in the vicinity of existing monitoring well MW-106A.

## **Task 2 - Organic Constituents and Metals Soil Sampling**

In order to address the data needs outlined above a total up to 57 soil samples will be collected from 31 locations across a total of six properties and within adjacent roadways in order to confirm TarGOST® results, complete the delineation of organic constituents and coal tar-impacts (e.g. staining, and solid tar), characterize the fill unit within and upgradient of the extent of impacts associated with OU1, refine the current extent of pyritic material to the west of the former acid plant, and develop the data sets necessary to evaluate potential risks to human health.

Sampling and analytical methods will be based on the specific objectives for each location. Drilling methods will involve the use of both direct-push and to a lesser extent, rotasonic drilling techniques. Rotasonic drilling methods will be employed at locations where shallow obstructions have historically proven to be an obstacle to continuous soil sampling, or where larger diameter borings are required for the installation of monitoring wells. A description of soil sampling proposed to address each of the related data needs is provided below.

Proposed sample locations for organic and metals analyses are illustrated separately on Figures 2 and 3 in context of soil contours representing the distribution of key constituents. Table 2 provides details on the analyses and specific data quality objectives for each proposed soil sampling location. In general, and unless noted below, each sample will be analyzed for VOCs, SVOCs, TAL Metals, and PCBs in accordance with the methods

specified in the revised QAPP (CH2M HILL, 2005; 2006a). Drilling and sampling methodologies at these 31 locations will be as follows:

- Up to twenty-one (24) direct-push borings and seven (7) rotasonic borings with continuous soil sampling will be advanced to depths corresponding with the top of the silty-clay aquitard or bedrock (if the silty-clay is not present) at Block 93 North, Central, South, Block 92.01, Block 94, and in northwestern and northeastern portions of the former Lever Brothers property. Up to three (3) soil samples will be collected from each location. Sample depth selection will be based on visual observations, PID screening results, and where available, TarGOST® response data. At each location one soil sample will be collected from the 0-2 foot bgs interval and a second will be collected from the most impacted interval between 2 and 10 feet bgs. If additional impacts are observed below a depth of 10 feet then a third sample may also be collected from the depth that corresponds with those impacts.
- In addition to parameters mentioned above any NAPL-impacted soil samples collected at the two (2) proposed borings in the northeastern portion of the former Lever Brothers property will also be collected for total petroleum hydrocarbon (TPH) fingerprinting using EPA Method 8100M.
- Due to the historical disturbances of soils within and immediately adjacent to the roadways as part of construction activities and/or the fact that these data are not intended to be used for the purpose of HHRA, samples collected at Block 92.01 and within the intersections of Gorge Road and River Road and Gorge Road and Old River Road may differ from those outlined above. Specifically, shallower samples collected for VOCs, SVOCs, and PCBs from the six (6) proposed borings within these areas may be collected from below 2 feet bgs and will target the most impacted depth based on visual and PID screening within the unsaturated soils (generally between 0 and 4 feet bgs). A second, deeper sample will be collected from most impacted saturated soil (generally below 4 feet bgs) interval.
- Soil sampling intervals for TAL metals at the six (6) borings within the roadways and at Block 92.01 will be selected based solely on visual observations and may differ from those intervals selected for the analysis of organics. Specifically, if reddish-purple soils are observed at any of these locations, depth intervals containing these soils will be targeted for sampling. If reddish-purple soils are observed to span the water table, one sample will be collected from the unsaturated zone and the second sample from the saturated zone. If one or more of these conditions does not exist, samples will be collected from the same intervals from which samples are to be collected for the analysis of organic parameters.

### **Task 3 - Arsenic Solid Phase Association Sampling**

At a total of ten (10) additional soil boring locations within suspected arsenic source areas and along three (3) separate transects that represent groundwater flow paths downgradient of these source areas up to 20 soil samples will be collected and analyzed using a 5-step sequential extraction process (SEP). Results of these analyses will determine the phases in which the arsenic in each soil sample is associated with, and whether the arsenic in soil at a given point along each of the key transects is mobile. The key groundwater flow transects and proposed locations for these samples are illustrated on Figure 4 in context of the groundwater isoconcentration contours for arsenic presented in the Draft RI Report and modified more recently as requested in the Agency Comments on the Draft RI Report.

A total of two (2) soil samples (a 'shallow' and a 'deeper' sample) will be collected for SEP analyses at each of the eight (8) proposed locations shown on Figure 4. All samples will be collected from saturated soils from within the elevation interval that corresponds with the saturated screen interval of the closest upgradient monitoring well(s) with the highest historical concentrations of arsenic in groundwater. Target sampling intervals for each of the proposed locations are summarized in Table 3 and details on sampling procedures are provided in the FSP (Attachment B).

Careful measures (as detailed in Appendix B) will be taken to preserve the oxidation state of the soil samples during collection and laboratory analysis. The phases of arsenic that will be quantified in each sample include non-specifically sorbed, specifically-sorbed, amorphous and poorly crystalline hydrous oxide bound, crystalline hydrous oxide bound, and residual arsenic in soil. The sequential extraction procedure will be performed using the methods outlined in Wenzel et al. (2000) with select project specific modifications. A copy of Wenzel et al. (2000) and the proposed changes to this method are provided in Attachment C of this Work Plan Addendum. SEP samples will also be sub-sampled in the laboratory and analyzed for total organic carbon (TOC) in accordance with the methods specified in the QAPP.

### **Task 4 - Monitoring Well Installations and Groundwater Grab Sampling**

In order to address select data needs outlined above, a total of thirteen (13) monitoring wells will be installed within Block 93 Central and South, Block 94, the former Lever Brothers property, the former Celotex property and within the intersections of Gorge and Old River Road and Gorge and River Road. In addition, one additional groundwater grab sample will be collected from Block 93 Central, from a temporary well point (TWP) for the purpose of providing additional data for risk characterization.

In general, monitoring wells and groundwater grabs will be installed at a subset of the locations proposed for soil sampling (see above). The specific data quality objectives and anticipated well construction information for proposed monitoring wells and the TWP are provided in Table 4. Locations are illustrated in context of the groundwater isoconcentration contours for benzene and arsenic on both Figures 5 and 6, respectively.

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- At each of the 13 proposed monitoring well locations, borings will be advanced using rotasonic drilling techniques. Each well will be constructed either as a 2-inch or 4-inch diameter PVC monitoring well (see Table 4) with a 0.020-slot 10 foot long screen with a 2-foot sump. All monitoring wells will be screened within the unconfined groundwater zone.
- For the five (5) proposed monitoring wells at Block 93 Central and South and Block 94 and one well on the former Celotex property (MW-135) the primary objective is to determine the dissolved phase impacts associated with Site-related NAPL or the mobility/recoverability in areas where NAPL is known to be present. At these locations, screened intervals will be designed to intersect the most impacted intervals observed during TarGOST® profiling, drilling and sampling.
- For the eight (8) remaining proposed monitoring wells within the roadways and at the former Lever Brothers and Celotex properties the primary objectives are to refine the nature and extent of arsenic impacts in groundwater and to further understand the mobility and fate and transport of arsenic downgradient of known source areas. At these locations, screened intervals will be designed to intersect the intervals of the saturated zone where the highest concentrations of arsenic in groundwater are believed to be located, based on existing upgradient and downgradient groundwater results for arsenic.
- Following their completion all monitoring wells will be developed at least 2 weeks prior to the initial sampling event.
- All newly-installed monitoring wells will be sampled as part of each of the proposed 2008 semi-annual groundwater sampling events (see below).
- The lateral locations and pertinent elevation information for each well will be surveyed relative to the established site datum by a Licensed New Jersey Surveyor.
- In order to provide sufficient groundwater data coverage for the HHRA at Block 93 Central during the completion of boring TWP-SB-41 at Block 93 Central, a temporary 1-inch diameter 0.020-slot pre-packed 5-foot long well screen will be installed to a depth of approximately 10 feet bgs (prior to advancing the boring deeper). Immediately following installation a groundwater sample will be collected from this location using low-flow sampling techniques. The sample from this location will be analyzed for volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs), and total and dissolved TAL metals in accordance with the revised QAPP.

### **Task 5 - 2008 Semi-Annual Groundwater Sampling**

Two groundwater sampling events involving newly installed wells and a subset of the existing monitoring well network is proposed in order to:



- 1.) Further assess the extent and fate and transport of coal tar constituents in groundwater;
- 2.) Further assess the groundwater geochemical conditions and fate and transport of arsenic across the site; and
- 3.) Collect data to support the evaluation of potential human health risk associated with groundwater at Block 93 Central and South and across OU1.

A summary of the wells proposed for each of the 2008 semi-annual groundwater sampling events, and the data quality objectives and proposed analytical parameters for each well and each event are provided in Table 5.

In order to refine the current understanding of the direction of groundwater flow and check for the presence of NAPL, a comprehensive round of depth to groundwater and product thickness measurements will be performed at the site using all existing and newly installed accessible monitoring points. These measurements will be collected by teams of field personnel over as short a time as possible during mid-tide conditions.

#### **Organic Constituents in Groundwater**

During both semi-annual groundwater events, samples will be collected from a total of thirty-six (36) monitoring wells across all properties (including all newly installed wells) and analyzed for VOCs and SVOCs. Samples collected from newly installed wells will also be analyzed for PCBs. Unless PCBs are detected in samples collected from these wells during the first semi-annual event this parameter will not be included in the analytical suite during the second event. Locations of the monitoring wells proposed for the analysis of these parameters are illustrated on Figure 5 and include three wells that were installed by other consultants and have not yet been sampled as part of the OU1 RI/FS activities (3Y-MW-2, MW-30 and MW-51).

#### **Geochemistry and Arsenic in Groundwater**

Additional analyses are proposed for both 2008 semi-annual groundwater monitoring events in order to understand the distribution of metals and the fate and transport of arsenic in groundwater. Locations of the monitoring wells proposed for the purpose of addressing these data needs are illustrated on Figure 6 in context of the isoconcentration contours for arsenic as presented in the Draft RI Report and recently revised in consideration of Agency comments on that report.

- During the first semi-annual groundwater sampling event, samples collected from the 36 wells specified above as well as an additional ten (10) wells (46 in total) will also be

analyzed for total and dissolved TAL metals, additional major ions<sup>1</sup>, alkalinity, and dissolved organic carbon (DOC).

- At nineteen (19) of the forty-six (46) monitoring well locations where groundwater samples will be collected during the first semi-annual sampling event, samples will also be collected for arsenic III and IV speciation using an NJDEP-approved ion chromatography method.
- During the second semi-annual groundwater sampling event groundwater samples collected from the thirty-six (36) monitoring wells for analysis of organic parameters specified above plus 2 additional newly installed (38 in total) will also be analyzed for total and dissolved arsenic, iron, and lead.

### **Task 6 - Shoreline and Wooden Bulkhead Characterization**

In order to refine the current understanding of the distribution of NAPL behind the wooden bulkhead and confirm the dimension of this feature a series of geophysical methods and borings with continuous soil sampling and visual observations are proposed for the area immediately behind the bulkhead and just beyond the southern and northern extents of the bulkhead.

In order to determine the depth and breadth of the wooden bulkhead a phased approach involving a series of surficial and down-hole geophysical methods will be employed at the Site. Details on each of borings proposed as part of the characterization of this area and their specific objectives are summarized in Table 6.

### **Soil Screening and Visual Characterization**

Due to the uncertainty of the distribution of NAPL adjacent to wooden bulkhead seven (7) additional borings will be completed immediately upgradient of bulkhead structure. The locations of the seven (7) proposed borings with continuous soil sampling, PID screening and visual observations are illustrated on Figure 7. These borings will allow for the determination of the vertical distribution of NAPL relative to the bulkhead structure. As discussed above, a subset of these locations will also allow for the collection of downhole vertical seismic profiling (VSP) data in order to confirm the depth of the bulkhead at various locations as well as for the installation of one monitoring well at the former Celotex property (MW-135) and nested piezometers at 3 locations (PZ-5, 6 and 7) at the Quanta property as part of Tasks 4 and 7, respectively.

- At each of the (7) locations rotasonic borings with continuous soil sampling will be advanced through the silty-clay aquitard to the top of the bedrock (anticipated depth of approximately 40 feet).

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<sup>1</sup> Additional major ions not included in the TAL Metals analysis include sulfate, sulfide, nitrate, and chloride.

- At each location a multi-case override system will be used during drilling to eliminate permanent surface casings and seal and isolate the shallow water bearing unit in order to prevent migration of groundwater and other potentially mobile substances into the silty-clay aquitard and below during and after drilling and well construction.

### **Geophysical Investigation**

Non-intrusive geophysical methods will be utilized to characterize the dimensions and characteristics of the known bulkhead and subsurface materials in the vicinity. The geophysical survey will utilize a phased approach involving surface geophysical techniques prior to employing more costly downhole techniques. Surface geophysical techniques to be employed include multi-frequency electromagnetic induction (EM), electrical resistivity (ER), and ground penetrating radar (GPR) profiling. In addition, a test of borehole GPR is proposed to be conducted during this phase, if surface techniques indicate a high probability of success.

Following completion of this first phase of work, a second phase involving down-hole geophysical survey work involving VSP and/or borehole GPR may be utilized in three (3) piezometer locations to further evaluate the dimensions and characteristics of the bulkhead.

The primary objectives of this work are as follows:

1. To characterize the depth and breadth of the wooden bulkhead; and
2. Determine if earlier generation bulkheads or structures may be present inboard from the wooden bulkhead.

Geophysical response may be affected by the presence of NAPL in the area, potential salt water intrusion near the shoreline, and other cultural debris that may be present. The field survey will involve a suite of techniques that will be adapted during implementation to attempt to best resolve these influences and identify the survey targets specified in the primary objectives.

Electrical and seismic methods provide an opportunity to evaluate the physical and electrical properties of subsurface materials. The suite of surface techniques including multi-frequency EM, ER, and GPR proposed to be used in the vicinity of the bulkhead in the area identified on Figure 7. Following evaluation of data collected during the surface surveys, a decision will be made concerning whether or not to conduct a test of borehole GPR at existing monitoring well MW-116DS. The borehole GPR survey will measure signal reflections from horizontally transmitted GPR signals that can be attributed to the bulkhead and will allow for an understanding as to whether the bulkhead depth is greater than depth of monitoring well MW-116DS and will provide information on the viability of using this method at newly proposed boring locations along the bulkhead.

Phase 1 geophysical surveys will also be used to refine the locations of borings to be drilled as part of the shoreline/bulkhead evaluation. These new boring are intended to further

optimize subsequent down-hole geophysical activities such that the likelihood of the successful imaging of the bottom of the bulkhead is increased.

The second phase of the geophysical investigation will involve borehole surveys in three deep piezometers proposed as part of the proposed GSI Evaluation (Task 7). At each of these locations vertical seismic profile (VSP) and possibly borehole GPR surveys will be performed.

If conducted, the borehole GPR surveys will be performed in the same manner as in the first stage. The VSP survey will be designed to detect disruptions of seismic ray paths due to the bulkhead obstruction. A sparker source will be located below the mud on the river side of the bulkhead. Hydrophone strings will be deployed in the three deep piezometers to measure the direct arrivals of seismic signals from the sparker source at all depths in the wells. Disruptions of the modeled ray paths that may be attributed to the bulkhead will be analyzed.

### **Task 7 - Groundwater-Surface Water Interaction Evaluation**

Proposed groundwater/surface water interaction (GSI) activities have been broken into three (3) main tasks which include:

- 1.) Locating and quantifying preferential groundwater discharge areas in OU2 through the implementation of a Trident Probe survey;
- 2.) Shallow pore water and surface water sampling at up to five (5) groundwater discharge locations identified during the Trident Probe survey; and
- 3.) Piezometer installation, pore water sampling, and hydraulic head measurements.

Specific Data Quality Objectives (DQOs) associated with each of these tasks are summarized in Table 7, and details on the scope of each task is provided in the following sections.

#### **Trident Probe Survey**

A Trident Probe survey will be conducted to identify areas where groundwater is upwelling to the surface water at OU2. A Trident Probe uses direct-push technology in conjunction with an integrated temperature sensor, conductivity sensor, and pore water sampler to screen sites for areas where ground water may be discharging to a surface water body. This is possible due to differences in temperature and conductivity between ground water and surface water. Spatial patterns of these two parameters can be used to identify areas of groundwater upwelling. The Trident Probe technology was developed by the Space and Naval Warfare Systems Center San Diego (SPAWAR). A technical report that includes hardware description, protocols, and procedures for the Trident Probe is provided as Attachment D.

In order to complete a comprehensive survey across the areas of OU2 that are downgradient of NAPL and dissolved phase impacts at OU1 groundwater, up to 11 transects have been developed at intervals of approximately 65 to 100 ft along the shoreline. Each transect is oriented perpendicular to the shoreline and extends to a distance of up to 400 feet. A maximum of 5 Trident Probe locations spaced at intervals between 75 and 100 ft will be sampled along each transect. The Trident Probe survey grid is illustrated in Figure 7. Data collection methods and equipment to be used are included in the Field Sampling Plan Addendum provided in Attachment B. The following activities will be performed for the Trident Probe survey:

- Up to fifty (55) Trident Probe locations (Figure 7) will be surveyed. Temperature and conductivity will be measured at each location at a depth of 2 feet below and 1 foot above the sediment water interface.
- The survey will be performed from a boat during ebbing tidal conditions, beginning at high tide and continuing until the surface water is no longer navigable by boat.
- At each location the boat will be anchored, and coordinates of the Trident Probe location will be recorded using a global positioning system (GPS) with sub-meter accuracy. In addition, the depth to the sediment surface will also be measured using a hand held acoustic sounder.
- The Trident Probe will be lowered through the water column and pushed into the sediment to a depth of approximately 2 foot below the sediment surface. Temperature and conductivity readings will be collected continuously from both above and below the sediment surface until stabilization of both parameters. Temperature and conductivity will also be measured at approximately 1 foot above the sediment water interface.

#### **Pore Water Sampling**

After completion of all Trident Probe locations, the temperature and conductivity data will be reviewed to determine those locations showing the greatest likelihood of groundwater discharge. Pore water samples will be collected from up to five (5) of those locations using the Trident Probe. In order to prevent infiltration of surface water into the probe during pore sampling while collecting samples from as close to the biologically active zone (0 to 1.0 feet) samples will be collected from approximately 0.5 to 1 feet below sediment surface. Details on the sample collection methods and equipment to be used are provided in the FSP Addendum provided in Attachment B. Data Quality Objectives (DQOs) are provided in Table 7. Pore water sampling will be performed as follows:

- Pore water sampling will be performed using the Trident Probe deployed from a boat during ebbing tidal conditions, beginning at high tide and continuing until the surface water is no longer navigable by boat.

- At each pore water sampling location, the boat will be repositioned at the original Trident Probe location using the GPS, and the depth to the sediment surface at each location will be measured using a hand held acoustic sounder prior to sampling.
- Prior to deployment, the Trident Probe will be adjusted such that sampler screen interval will span a depth of 0.5 to 1 ft. below the sediment surface. A metal plate at the top of the Trident probe will serve to guide the probe to the designated depth and prevent intrusion of surface water into the sampling probe during pore water sampling.
- After lowering the Trident Probe through the water column and pushing it into the sediment to a depth of no greater than 1 ft. below the sediment surface, the probe will be stabilized at the water surface and pore water will be collected using a peristaltic pump and dedicated polyethylene tubing.
- Pore water samples will be collected and analyzed ex-situ in the field for pH, ORP, and DO. These readings will also help to confirm if infiltration of surface water into the pore water sample is occurring as a result of sampling.
- Pore water samples will also be collected for the laboratory analysis of VOCs, SVOCs, and dissolved arsenic in accordance with the methods specified in the revised QAPP.
- At each of the five (5) pore water sampling locations, samples will also be collected in an oxygen-free environment for arsenic speciation using an NJDEP-approved ion chromatography method specified in the revisions to the QAPP provided herein as Attachment A. This will ensure the preservation of the oxidation state of the pore water prior to analysis at the lab. Details on this procedure are provided in the FSP Addendum (Attachment B).
- At each of the five (5) pore water sampling locations, surface water samples will also be collected for laboratory analysis of VOCs, SVOCs and dissolved arsenic.

#### **OU1 Piezometer Installation**

At three (3) of the borings installed behind the wooden bulkhead as part of the shoreline and wooden bulkhead characterization, nested piezometers will be installed in order to collect hydraulic head information along the shoreline adjacent to, and to the north and south of the wooden bulkhead and at varying depths within OU1. These data will be used in conjunction the hydraulic head information collected at the proposed nested drive-point piezometers within OU2 (see below) and at other monitoring wells within OU1 to determine flow paths from source areas at OU1 to pore water at varying depths at OU2. The approximate locations of the proposed upland piezometer nests are illustrated on Figure 7.

- At each OU1 piezometer nest locations a total of three piezometers with discrete 2 foot long screens will be installed within drilled boreholes to depths of approximately 35, 20 and 5 feet below ground surface.

- Each piezometer will consist of 1 to 2-inch diameter PVC with a 2 ft. long 0.02-slot screen with an appropriate sand pack and seal. Due to the density of existing groundwater data in these areas piezometers groundwater samples will not be collected from the OU1 nested piezometers as part of this scope of work.

#### **OU2 Piezometer Installation and Sampling and Hydraulic Head Measurements**

Following the completion of the Trident Probe survey, nested drive-point piezometers will be installed at five (5) locations at varying depths within OU2 in order to collect pore water samples and hydraulic head information downgradient of dissolved phase impacts at OU1. The approximate locations of the proposed piezometer nests are illustrated on Figure 7. Data Quality Objectives (DQOs) for this work are provided in Table 7. Proposed locations have been selected to cover the near shore area in front of the wooden bulkhead at increasing distance from the shoreline as well as to the south and north of the wooden bulkhead. Final locations may be adjusted based on the results of the geophysical investigations in the area of the bulkhead or to target groundwater upwelling areas identified in the vicinity of each of these proposed during the Trident Probe survey. The following activities will be performed:

- At each piezometer nest a total of three drive-point piezometers will be installed using a slide-hammer to depths of 25, 15 and 5 feet below sediment surface.
- Each piezometer will be installed during low tide when the near shore mud flats can be accessed using temporary plywood walkways. Piezometer tips will consist of 3/4 inch stainless steel 0.5 ft. long screened probe coupled to 1/2 inch ID Teflon® sample tubing, and driven using 3/4 inch steel pipe extensions.
- Following installation, the depth to water will be measured inside the Teflon® tubing within each piezometer using a small diameter (1/4 inch) electronic water level probe. The elevation of each probe will be measured relative to a known benchmark at OU1 using a survey rod and level. The lateral location of each piezometer cluster will be recorded using a GPS with sub-meter accuracy.
- Pore water samples will be collected from each of the piezometers by purging a total of one piezometer volume of pore water from within the Teflon tubing into a flow-thru cell. Once the flow-thru cell is oxygen free, DO, ORP, pH, temperature and conductivity readings will then be taken within the flow-thru cell until stabilization has occurred.
- Upon stabilization of the parameters pore water samples will be collected for VOCs, SVOCs, and dissolved arsenic in accordance with the methods specified in the revised QAPP.
- Following the installation of the nested piezometers within OU2 depth to water measurements will be collected from all newly installed piezometers within OU1 and OU2 up to 6 times over both high and low tide conditions over a period of one week. All

measurements will be collected and in conjunction with water elevation data at the existing staff gauge within the Hudson River and at all available wells at OU1 adjacent to the shoreline.

### **Quality Control (QA/QC)**

QA/QC samples and field procedures will be collected and performed in accordance with the revised OU1 QAPP (CH2M HILL, 2005; 2006a). All data received from the laboratory will be reviewed by a qualified chemist and validated in context of the revised QAPP and the established Data Quality Objectives (DQOs) for the tasks as specified in the attached Tables 1 through 7. An addendum to the QAPP has been prepared for the collection of groundwater samples being analyzed for sulfate, nitrate, chloride, alkalinity, DOC, arsenic III and V speciation and arsenic SEP analyses and is included as Attachment A.

### **Data Evaluations and Presentation**

The data collected during the SRI and the first semi-annual groundwater sampling event will be evaluated in conjunction with existing applicable data previously presented in the Draft RI Report (CH2M HILL, 2007a) to determine the extent and mobility of NAPL in the vicinity Block 93 North, Central and South. In addition, these data will be used to determine the lateral and vertical extent and fate and transport of OU1-related constituents in soil and groundwater throughout the site. These data will be used to confirm or revise the current conceptual site model as presented in the Draft RI Report.

Where appropriate, existing and newly collected analytical data meeting the applicable quality control criteria specified in the Revised QAPP (CH2M HILL, 2005; 2006a) will also be incorporated into an HHRA for both the Block 93 Central and Block 93 South properties. Existing risk assessment calculations for site-wide groundwater and properties where additional data will be collected will be evaluated in context of the newly collected data and updated as appropriate.

The results of the SRI and the first semi-annual groundwater sampling event as well as the subsequent data evaluations and revisions to the HHRA will be provided to the USEPA as a Draft Supplemental RI Report for OU1. The report will be prepared in accordance with original RI/FS Work Plan (Parsons, 2005a). This report will serve to supplement and where applicable, update the necessary components of the Final RI Report for OU1.

Results from the second semi-annual groundwater event will be summarized in a brief letter report which will be forwarded to the Agencies along with all results.

### **Schedule**

Procurement, mobilization, and implementation of the work plan would begin immediately following EPA authorization to proceed. The approximate durations of tasks associated



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with this work plan are presented below. Upon review and verbal approval of the Work Plan and its attachments, an updated project schedule and milestone chart will be developed and submitted.

Task	Estimated Duration
Review and Authorization from EPA to proceed with Remedial Investigation/ Feasibility Study Work Plan Addendum No. 4	2 weeks
Procurement, mobilization and implementation (not including second semi-annual groundwater sampling event)	16 weeks
Laboratory Analysis of Samples	4 weeks
Data Validation of Laboratory Results	3 weeks
Data Evaluation and Summary	12 weeks

Following the receipt of comments and agreement from the USEPA and NJDEP on the Work Plan Addendum proposed herein field activities will be initiated.

If you have any questions or concerns, please feel free to contact me at 215-640-9087.

Sincerely,

CH2M HILL



Stephen J. Zarlinski, P.E.  
Senior Project Manager

Attachments

Cc: Robert Hayton (NJDEP)  
Helen Fahy (Honeywell)  
Richard Kampf (ESAG)

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## Tables

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**TABLE 1**  
**SUPPLEMENTAL REMEDIAL INVESTIGATION**  
**TarGOST PROFILING LOCATIONS**  
 May 2008  
 Quanta Resources Superfund Site  
 Edgewater, New Jersey

Property	Proposed Location/ TarGOST® Boring ID		Method	Approximate Proposed Depth (ft.)	<sup>2</sup> Data Quality Objectives (DQO)
	E-W Axis	N-S Axis			
Block 93 Central	TL13.5	12.75	GeoProbe+ TarGOST	30	1.) cost-effectively define NAPL extents southwest of NAPL observed at SB-30 and SB-27
Block 93 Central	TL12.5	10.5	GeoProbe+ TarGOST	30	1.) evaluate NAPL connection between NZ-1 and NZ-4
Block 93 Central	TL13.5	10.5	GeoProbe+ TarGOST	30	1.) evaluate NAPL connection between NZ-1 and NZ-4
Block 93 North	TL14	12.25	TarGOST	30	1.) cost-effectively define NAPL extents south of NAPL observed at SB-30 and SB-27
Block 93 North	TL14	13.25	GeoProbe+ TarGOST	30	1.) cost-effectively define NAPL extents west of NAPL observed at SB-30
Block 93 North	TL14.5	11.75	TarGOST	30	1.) cost-effectively define NAPL extents east of NAPL observed at SB-30 and SB-27
Block 93 South	TL09.5	10.5	GeoProbe+ TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-10.75
Block 93 South	TL09.5	11.25	TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-10.75
Block 93 South	TL10	11.25	TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-10.75
Block 93 South	TL10.5	10.5	GeoProbe+ TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-10.75
Block 93 South	TL10.5	11.25	GeoProbe+ TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-10.75
Block 93 South	TL11	10.5	TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-10.75
Block 93 South	TL11	11.25	TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-10.75
Block 93 South	TL11	11.75	TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-10.75
Block 93 South	TL11.5	10.5	TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-10.75
Block 93 South	TL11.5	11.25	GeoProbe+ TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-10.75
Lever Brothers	TL10	06.5	TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-08.5 and TL10-07.5 in northwestern portion of the former Lever Brothers property
Lever Brothers	TL10	07.5	GeoProbe+ TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-08.5 and TL10-07.5 in northwestern portion of the former Lever Brothers property
Lever Brothers	TL10	09	TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-08.5 and TL10-07.5 in northwestern portion of the former Lever Brothers property
Lever Brothers	TL10.5	09.5	GeoProbe+ TarGOST	30	1.) cost-effectively define NAPL extents to the south and west of TL12-08.5 and TL10-07.5 in northwestern portion of the former Lever Brothers property
Lever Brothers	TL12	00.5	GeoProbe+ TarGOST	30	1.) confirm NAPL delineation in northeast corner of former Lever Bros. property, and 2.) determine whether product in vicinity of MW-106A is NAPL <sub>coal tar</sub> .
Lever Brothers	TL12	01.5	GeoProbe+ TarGOST	30	1.) confirm NAPL delineation in northeast corner of former Lever Bros. property, and 2.) determine whether product in vicinity of MW-106A is NAPL <sub>coal tar</sub> .

**Notes:**

1. All TarGOST® profile locations are considered Dynamic Profile Locations (DPL) - At all DPLs where evidence of coal tar is detected using TarGOST® investigation of the coal tar using additional TarGOST® borings will be made by stepping out a maximum of 100 feet in four directions along the established grid axes until coal tar extents are fully delineated or the extents of the property boundaries are reached, whichever occurs first.

2. Data Quality Objective for ALL TarGOST® borings is to cost-effectively delineate the boundary of coal tar within the Block 93 and Lever Brothers properties. This will help to determine risks associated with the presence of NAPL and the most cost-effective means of mitigating impacts.

**TABLE 2**  
**SUPPLEMENTAL REMEDIAL INVESTIGATION**  
**SOIL SAMPLING AND ANALYSIS PLAN FOR COAL TAR CONSTITUENTS AND METALS**  
 May 2008  
 Quanta Resources Superfund Site  
 Edgewater, New Jersey

Property	Proposed Location/ Boring ID		Method	Laboratory Analytical for Soil Samples and Approximate Depths (ft.)								GW Grab for VOC, SVOC, PCB, & TAL Metals (dissolved + total)	Data Quality Objectives (DQO)
				VOC		SVOC		PCBs		TPH Fingerprint			
	0-2	>2		0-2	>2	0-2	>2	0-2	>2	0-2	>2		
Block 92.01	SB-52		Direct-Push	2		2		2			2		1.) confirm extent of coal tar constituents in soil in vicinity of former ASTs once located at the intersection of Gorge and River Roads; and 2.) confirm extent of arsenic and lead soil associated with pyritic material to the east.
Block 93 Central	MW-127		Sonic	1	1	1	1	1	1		1	1	1.) delineate extent of coal tar constituents in soil at Block 93 Central; 2.) delineate extent of arsenic in soil at Block 93 Central; and 3.) Provide soil data for Block 93 Central HHRA;
Block 93 Central	SB-40		Direct-Push	1	1	1	1	1	1		1	1	1.) delineate extent of coal tar constituents in soil at Block 93 Central; 2.) delineate extent of arsenic in soil at Block 93 Central; and 3.) Provide soil data for Block 93 Central HHRA;
Block 93 Central	SB-42		Direct-Push	1	1	1	1	1	1		1	1	1.) delineate extent of coal tar constituents in soil at Block 93 Central; 2.) delineate extent of arsenic in soil at Block 93 Central; and 3.) Provide soil data for Block 93 Central HHRA;
Block 93 Central	SB-43		Direct-Push	1	1	1	1	1	1		1	1	1.) delineate extent of coal tar constituents in soil at Block 93 Central; 2.) delineate extent of arsenic in soil at Block 93 Central; and 3.) Provide soil data for Block 93 Central HHRA;
Block 93 Central	SB-44		Direct-Push	1	1	1	1	1	1		1	1	1.) delineate extent of coal tar constituents in soil at Block 93 Central; 2.) delineate extent of arsenic in soil at Block 93 Central; and 3.) Provide soil data for Block 93 Central HHRA;
Block 93 Central	TL13.5	12.75	Direct-Push+ TarGOST	1	1	1	1	1	1		1	1	1.) confirm TarGOST® results; 2.) delineate extent of coal tar constituents in soil at Block 93 Central; and 3.) Provide soil data for Block 93 Central HHRA.
Block 93 Central	TWP-SB-41		Direct-Push	1	1	1	1	1	1		1	1	1.) delineate extent of coal tar constituents in soil at Block 93 Central; 2.) delineate extent of arsenic in soil at Block 93 Central; and 3.) Provide soil data for Block 93 Central HHRA;
Block 93 Central	TL12.5	10.5	Direct-Push+ TarGOST	1	1	1	1	1	1		1	1	1.) confirm TarGOST® results; 4.) evaluate extent of elevated arsenic concentrations (>100 ppm) in historic fill along eastern border of the Block 93 North property to the south TL14-10.75 and SB-22.
Block 93 Central	TL13.5	10.5	Direct-Push+ TarGOST	1	1	1	1	1	1		1	1	1.) confirm TarGOST™ results; 2.) delineate extent of coal tar constituents in soil along the eastern border of the Block 93 North property; and 3.) evaluate extent of elevated arsenic concentrations (>100 ppm) along eastern border of the Block 93 North property to the south of TL14-10.75 and SB-22.
Block 93 North	TL14	13.25	Direct-Push+ TarGOST	1	1	1	1	1	1		1	1	1.) confirm TarGOST™ results; 2.) delineate extent of coal tar constituents in soil along the western border of the Block 93 North property; and 3.) evaluate arsenic concentrations along western border of the Block 93 North property; 4.) Quantify dissolved-phase organic contaminant concentrations north of NAPL Zone 4; 5.) Supplement additional monitoring well groundwater data for property-specific HHRA for Block 93 Central;
Block 93 South	MW-123		Sonic	1		1		1			1		1.) delineate extent of coal tar constituents in shallow soil at Block 93 South; and 2.) provide soil data for Block 93 South HHRA
Block 93 South	MW-124		Sonic	1	1	1	1	1	1		1	1	1.) delineate extent of coal tar constituents in soil at Block 93 South; and 2.) provide soil data for Block 93 South HHRA
Block 93 South	SB-47		Direct-Push	1	1	1	1	1	1		1	1	1.) delineate extent of coal tar constituents in soil at Block 93 South; and 2.) provide soil data for Block 93 South HHRA
Block 93 South	SB-48		Direct-Push	1	1	1	1	1	1		1	1	1.) delineate extent of coal tar constituents in soil at Block 93 South; and 2.) provide soil data for Block 93 South HHRA
Block 93 South	TL09.5	10.5	Direct-Push+ TarGOST	1	1	1	1	1	1		1	1	1.) confirm TarGOST® results; 2.) delineate extent of coal tar constituents in soil at Block 93 South; and 3.) provide soil data for Block 93 South HHRA
Block 93 South	TL10.5	10.5	Direct-Push+ TarGOST	1	1	1	1	1	1		1	1	1.) confirm TarGOST® results; 2.) delineate extent of coal tar constituents in soil at Block 93 South; and 3.) provide soil data for Block 93 South HHRA
Block 93 South	TL10.5	11.25	Direct-Push+ TarGOST	1	1	1	1	1	1		1	1	1.) confirm TarGOST® results; 2.) delineate extent of coal tar constituents in soil at Block 93 South; and 3.) provide soil data for Block 93 South HHRA
Block 93 South	TL11.5	11.25	Direct-Push+ TarGOST	1	1	1	1	1	1		1	1	1.) confirm TarGOST® results; 2.) delineate extent of coal tar constituents in soil at Block 93 South; and 3.) provide soil data for Block 93 South HHRA
Block 94	MW-128		Sonic	1	1	1	1	1	1		1	1	1.) confirm extent of coal tar constituents in soil west of Old River Road; and 2.) evaluate arsenic concentrations in fill west of Old River Road.
Block 94	MW-129		Sonic	1	1	1	1	1	1		1	1	1.) confirm extent of coal tar constituents in soil west of Old River Road; and 2.) evaluate arsenic concentrations in fill west of Old River Road.
Block 94	SB-39		Direct-Push	1	1	1	1	1	1		1	1	1.) confirm extent of coal tar constituents in soil west of Old River Road; and 2.) evaluate arsenic concentrations in fill west of Old River Road.
Gorge/Old River Rd	MW-125		Sonic	2		2		2			2		1.) delineate extent of coal tar constituents in soil north of MW-111 series wells; 2.) delineate extent of arsenic in soil north of MW-111 series wells; and 3.) evaluate fill conditions.
Lever Brothers	TL10	07.5	Direct-Push+ TarGOST	1		1		1			1		1.) confirm TarGOST® results; and 2.) delineate extent of coal tar constituents in the northwestern corner of the former Lever Brothers property;
Lever Brothers	TL10.5	09.5	Direct-Push+ TarGOST	1		1		1			1		1.) confirm TarGOST® results; and 2.) delineate extent of coal tar constituents in the northwestern corner of the former Lever Brothers property;
Lever Brothers	TL12	00.5	Direct-Push+ TarGOST	1		1		1		1	1		1.) confirm TarGOST® results; 2.) confirm extent of coal tar constituents in soil in the northeast corner of the former Lever Brothers property; and 3.) evaluate type of product observed in boring from MW-106A which indicates non-coal tar impacts (no PAHs in highest PID screening result interval)
Lever Brothers	TL12	01.5	Direct-Push+ TarGOST	1		1		1		1	1		1.) confirm TarGOST® results; 2.) confirm extent of coal tar constituents in soil in the northeast corner of the former Lever Brothers property; and 3.) evaluate type of product observed in boring from MW-106A which indicates non-coal tar impacts (no PAHs in highest PID screening result interval)
River/Gorge Rd	MW-126		Sonic	2		2		2			2		1.) confirm extent of coal tar constituents in soil in vicinity of former ASTs once located at the intersection of Gorge and River Roads; and 2.) confirm extent of arsenic and lead soil associated with pyritic material to the east.
River/Gorge Rd	SB-49		Direct-Push	2		2		2			2		1.) confirm extent of coal tar constituents in soil in vicinity of former ASTs once located at the intersection of Gorge and River Roads; and 2.) confirm extent of arsenic and lead soil associated with pyritic material to the east.
River/Gorge Rd	SB-50		Direct-Push	2		2		2			2		1.) confirm extent of coal tar constituents in soil in vicinity of former ASTs once located at the intersection of Gorge and River Roads; and 2.) confirm extent of arsenic and lead soil associated with pyritic material to the east.
River/Gorge Rd	SB-51		Direct-Push	2		2		2			2		1.) confirm extent of coal tar constituents in soil in vicinity of former ASTs once located at the intersection of Gorge and River Roads; and 2.) confirm extent of arsenic and lead soil associated with pyritic material to the east.

**Notes:**

1. Specific laboratory analytical methods and analyte lists are provided in the revised Quality Assurance Project Plan (QAPP) (CH2M Hill, 2005; 2006a)

TAL Metals: Target Analyte Metals, VOCs: volatile organic compounds, SVOCs: semi-volatile organic compounds, PCBs: polychlorinated biphenyls

QA/QC: Samples will be taken at the frequency specified in the revised QAPP (CH2M Hill, 2005; 2006a) (Both MS/MSD and Field Duplicates = 1 per 20 samples (5%) per matrix)

2. At locations where the TarGOST® delineation method will be used in conjunction with soil sampling (Direct-Push+ TarGOST®), soil sampling will be done following the TarGOST work at that location and sampling intervals for VOCs, SVOCs, and PCBs will target the most impacted intervals based on TarGOST® results

**TABLE 3**  
**SUPPLEMENTAL REMEDIAL INVESTIGATION**  
**SEQUENTIAL EXTRACTION PROCEDURE FOR ARSENIC**  
**SOIL SAMPLING AND ANALYSIS PLAN**  
 May 2008  
 Quanta Resources Superfund Site  
 Edgewater, New Jersey

Arsenic Attenuation Transect	Proposed Location/ Boring ID	Method	Property	<sup>1</sup> Laboratory Analytical for Soil Samples and Approximate Depths (ft.)		<sup>1</sup> Sequential Extraction Procedure (SEP) for Arsenic		Data Quality Objectives (DQO)
				Total Arsenic and Total Organic Carbon (TOC)				
				<sup>2</sup> shallow	<sup>2</sup> deeper	<sup>2</sup> shallow	<sup>2</sup> deeper	
High As Area	SB-53	GeoProbe	Quanta	2-12	16-17	2-12	16-17	1.) Confirm the mobility and attenuation of arsenic within the pyritic waste material located within Geochemical Zone 1A.
	SB-54	Sonic	Fmr. Celotex	4-10	22-23	4-10	22-23	1.) Confirm the mobility and attenuation of arsenic within the pyritic waste material located within Geochemical Zone 1A
Transect 1	MW-126	Sonic	River/Gorge Rd	4-10	22-23	4-10	22-23	1.) Confirm the mobility and attenuation of arsenic along Transect 1, hydraulically downgradientthe pyritic waste material and along the boundary between Geochemical zones 1a and 2; 2.) Determine whether there is connection between dissolved As associated with pyritic material (MW-N series wells) and that observed at the MW-111 series wells.
	MW-128	Sonic	Block 94	4-10	22-23	4-10	22-23	1.) Determine the presence and mobility and attenuation of arsenic along Transect 1; 2.) If groundwater flow directions trend eastward from Block 93 North, determine whether As, if present, has migrated from Block 93 Northto Block 94; 3.) If groundwater flow directions trend eastward from Block 94, determine whether As, if present, is a potential source of arsenic observed at Block 93 North.
Transect 2	MW-133	Sonic	Fmr. Celotex	10-15	17-18	10-15	17-18	1.) Confirm the mobility and attenuation of arsenic along Transect 2, hydraulically downgradientthe pyritic waste material and along the boundary between Geochemical Zones 1A and 5; 2.) Determine whether there is a connection between dissolved As associated with pyritic material observed in the northwest corner of the Quanta property and that observed hydraulically downgradientat MW-Q.
	MW-134	Sonic	Fmr. Celotex	10-15	17-18	10-15	17-18	1.) Confirm the mobility and attenuation of arsenic along Transect 2, hydraulically downgradientthe pyritic waste material and along the boundary between Geochemical zones 5 and 4; 2.) Determine whether there is a connection between dissolved As associated with pyritic material observed in the northwest corner of the Quanta property and that observed hydraulically downgradientadjacent to the River at MW-C; 3.) Determine if arsenic observed at MW-C attenuates prior to reaching the River.
Transect 3	MW-130A & B	Sonic	Lever Brothers	5-15	20-21	5-15	20-21	1.) Confirm the mobility and attenuation of arsenic in along Transect 3, hydraulically downgradient of the MW-114 series wells between Geochemical Zones 3 and 1B; 2.) Determine whether there is connection between dissolved As associated with pyritic material observed in the northwest corner of the Quanta property and that observed hydraulically downgradientin the vicinity of MW-107 series wells.
	SB-55	Sonic	Lever Brothers	3-13	19-20	3-13	19-20	1.) Confirm the mobility and attenuation of arsenic within the suspected source area along Transect 3, hydraulically downgradient of the MW-114 series wells within Geochemical Zone 1B.
	MW-131	Sonic	Lever Brothers	3-13	19-20	3-13	19-20	1.) Confirm the mobility and attenuation of arsenic along Transect 3, hydraulically downgradientthe of the suspected source area at the MW-107 series wells and along the boundary between Geochemical Zones 3 and 5; 2.) Determine whether there is connection between dissolved As associated with the MW-107 series wells and the River.
	MW-132	Sonic	Lever Brothers	3-13	19-20	3-13	19-20	1.) Confirm the mobility and attenuation of arsenic along Transect 3, hydraulically downgradientthe of the suspected source area at the MW-107 series wells and along he boundary between Geochemical Zones 3 and 5; 2.) Determine whether there is connection between dissolved As associated with the MW-107 series and/or that observed at newly installed MW-131 and the River.

**Notes:**

1. The Sequential Extraction Procedure (SEP) for arsenic includes analysis of arsenic in each of the extracts resulting from a 5-step extraction process that aims to quantify the portion of total arsenic concentrations of each soil sample that are in the following five forms: 1.) non-specifically sorbed; 2.) specifically-sorbed; 3.) amorphous and poorly crystalline hydrous oxide bound; 4.) crystalline hydrous oxide bound; and 5.) residual arsenic
2. Target sample intervals are based on the screen interval elevation of the nearest upgradient or downgradient well where elevated arsenic has historically been observed. 'Shallow' and 'deeper' samples will be collected across the 2-foot span within the saturated zone of the target interval specified above that indicates the greatest abundance of visual evidence of arsenic containing materials (e.g. slag, cinders, coal or reddish-purple soils). If no visual impacts are observed the sample will be collected from the midpoint of the intervals specified above.
3. QA/QC Samples will be taken at the frequency specified in the revised QAPP (CH2M Hill, 2005; 2006a) (Both MS/MSD and Field Duplicates = 1 per 20 samples (5%) per matrix)

**TABLE 4**  
**SUPPLEMENTAL REMEDIAL INVESTIGATION**  
**PROPOSED MONITORING WELLS**  
 May 2008  
 Quanta Resources Superfund Site  
 Edgewater, New Jersey

Property/ Location	Proposed Monitoring Well ID	Method	Laboratory Analytical Soil Sampling Information	Approximate Anticipated Well		Data Quality Objective (DQO)
				Top (ft. bgs)	Bottom (ft. bgs)	
Block 93 Central	MW-127	Sonic 2-inch Monitoring Well	Table 2	6	16	1.) Define the western extent of dissolved-phase organic contamination associated with NZ-4; 2.) define geochemical zones and arsenic in groundwater
Block 93 South	MW-123	Sonic 4-inch Monitoring Well	Table 2	6	16	1.) Monitor plume conditions immediately in the vicinity of NZ-4; 2.) define geochemical zones and arsenic in groundwater; and 3.) determine if NAPL observed in TarGOST® boring TL12-10.75 at 12-16 ft. bgs is free-phase (i.e. will accumulate within the well).
Block 93 South	MW-124	Sonic 2-inch Monitoring Well	Table 2	6	16	1.) Define the southwestern extent of dissolved-phase organic contamination associated with NZ-4; 2.) define geochemical zones and arsenic in groundwater
Block 94	MW-128	Sonic 2-inch Monitoring Well	Table 2 & 3	5	15	1.) Define geochemical zones and extent of arsenic west of the MW-111 series wells; 2.) Determine groundwater flow direction between Block 93 and Block 94; 3.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transient 1; 4.) Define the extent of dissolved-phase organic constituents west of Block 93 North; and 5.) Understand mobility (speciation) of arsenic in groundwater.
Block 94	MW-129	Sonic 2-inch Monitoring Well	Table 2	5	15	1.) Define the extent of dissolved-phase organic constituents west of Block 93 North; 2.) Define geochemical zones and extent of arsenic west of the MW-111 series wells; and 3.) Determine groundwater flow direction between Block 93 and Block 94.
Fmr Celotex	MW-133	Sonic 2-inch Monitoring Well	Table 3	10	20	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transient 2 downgradient of Geochemical Zone 1A; 2.) Determine whether there is a connection between dissolved As associated with pyritic material observed in the northwest corner of the Quanta property and that observed hydraulically downgradient at MW-0; and 3.) Refine the boundaries of Geochemical Zones 1A, 4 and 5; and 4.) Understand mobility (speciation) of arsenic in groundwater.
Fmr Celotex	MW-134	Sonic 2-inch Monitoring Well	Table 3	15	25	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transient 2 at the boundary between Geochemical Zones 5 and 4; 2.) Determine whether there is a connection between dissolved As associated with pyritic material observed in the northwest corner of the Quanta property and that observed hydraulically downgradient adjacent to the River at MW-C; 3.) Determine if arsenic observed at MW-C attenuates prior to reaching the shoreline of the River; 4.) Refine the boundaries of Geochemical Zones 4 and 5; and 5.) Determine if NAPL observed at the former Celotex property in NAPL Zone NZ-5 is mobile (i.e. recoverable); and 5.) Understand mobility (speciation) of arsenic in groundwater.
Fmr Celotex	MW-135	Sonic 4-inch Monitoring Well	no sampling proposed	15	25	1.) Determine if NAPL observed at the former Celotex property in NAPL Zone NZ-5 is mobile (i.e. recoverable) and whether it is connected to NAPL at NZ-2;



**TABLE 4**  
**SUPPLEMENTAL REMEDIAL INVESTIGATION**  
**PROPOSED MONITORING WELLS**

May 2008

Quanta Resources Superfund Site  
 Edgewater, New Jersey

Property/ Location	Proposed Monitoring Well ID	Method	Laboratory Analytical Soil Sampling Information	Approximate Anticipated Well		Data Quality Objective (DQO)
				Top (ft. bgs)	Bottom (ft. bgs)	
Fmr Lever Bros.	MW-130A	Sonic 2-inch Monitoring Well	Table 3	4	14	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 3 downgradient of Geochemical Zone 3 and whether there is connection between dissolved As observed at the MW-114 series wells and that observed at the MW-107 series wells; 2.) Refine the extent of dissolved-phase organic constituents south of former OU1 operations in shallow unconfined unit (water table); and 3.) Refine the boundaries of Geochemical Zones 3 and 1B; and 4.) Understand mobility (speciation) of arsenic in groundwater.
Fmr Lever Bros.	MW-130B	Sonic 2-inch Monitoring Well	Table 3	15	25	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 3 downgradient of Geochemical Zone 3 and whether there is connection between dissolved As observed at the MW-114 series wells and that observed at the MW-107 series wells; 2.) Refine the extent of dissolved-phase organic constituents south of former OU1 operations in deeper unconfined unit (water table); and 3.) Refine the boundaries of Geochemical Zones 3 and 1B; and 4.) Understand mobility (speciation) of arsenic in groundwater.
Fmr Lever Bros.	MW-131	Sonic 2-inch Monitoring Well	Table 3	4	14	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 3 downgradient of Geochemical Zone 1B; 2.) Determine the extent of dissolved-phase organic constituents and arsenic in groundwater hydraulically downgradient of the MW-107 series wells; and 3.) Refine the boundaries of Geochemical Zones 1B, 3 and 5.
Fmr Lever Bros.	MW-132	Sonic 2-inch Monitoring Well	Table 3	4	14	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 3 downgradient of Geochemical Zone 1B and immediately upgradient of the River; 2.) Determine the extent of dissolved-phase impacts south of elevated arsenic and coal tar constituents in groundwater hydraulically downgradient of the MW-107 series wells; 3.) Determine if dissolved-phase organic constituents and arsenic are reaching the shoreline of the River; and 4.) Refine the boundaries of Geochemical Zones 4 and 5; and 5.) Understand mobility (speciation) of arsenic in groundwater.
Gorge/Old River Rd	MW-125	Sonic 2-inch Monitoring Well	Table 3	5	15	1.) Define the extent of dissolved-phase organic constituents on the upgradient edge of former OU1 operations; and 2.) Define geochemical zones and extent of arsenic northwest of the MW-111 series wells
Gorge/River Rd	MW-126	Sonic 2-inch Monitoring Well	Table 2 & 3	8	18	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 1, hydraulically downgradient the pyritic waste material and along the boundary between Geochemical zones 1A and 2; 2.) Determine whether there is connection between dissolved As associated with pyritic material (MW-N series wells) and that observed at the MW-111 series wells; 3.) Refine the boundaries of Geochemical Zones 2 and 5; 4.) Refine the extent of dissolved-phase organic constituents within the intersection of Gorge and River Roads (near former ASTs); 5.) Confirm the direction of groundwater flow between the pyritic waste material and Block 93 North; and 6.) Understand mobility (speciation) of arsenic in groundwater.

**Notes:**

1. All 2 and 4-inch diameter monitoring wells will be constructed as PVC wells with approximately 10-feet of 0.020 slot well screen and a 2-foot long sump at the base of the screen.
2. Exact screen depths will depend on NAPL observations or SEP Sampling intervals where applicable.
3. Anticipated well construction depths have been developed based on existing soil, groundwater and TarGOST® data in the vicinity of the proposed well location, and are designed to address the specific objective of each well listed above.

TABLE 5  
SUPPLEMENTAL REMEDIAL INVESTIGATION SEMI-ANNUAL  
GROUNDWATER SAMPLING AND ANALYSIS PLAN  
May 2008  
Quanta Resources Superfund Site  
Edgewater, New Jersey

Monitoring Well ID	New or Existing Monitoring Well	Property	Laboratory Analytical Samples - All Semi-Annual Events				Laboratory Analytical Samples - First Semi-Annual Event Only							Data Quality Objective (DQO)
			<sup>1</sup> VOC	<sup>2</sup> SVOC	<sup>3</sup> Dissolved As, Pb, Fe	<sup>4</sup> Total As, Pb, Fe	<sup>5</sup> PCBs	Dissolved TAL Metals (field filtered)	Total TAL Metals (non-filtered)	As III and IV Speciation (non-filtered)	<sup>6</sup> Additional Major Ions (non-filtered)	Alkalinity	Dissolved Organic Carbon	
MW-114A	Existing	115 River Rd.	1	1	1	1		1	1	1	1	1	1	1.) Monitor plume stability in vicinity of NZ-1 and adjacent to occupied building; 2.) confirm definition of geochemical zones and arsenic in groundwater; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-114B	Existing	115 River Rd.	1	1	1	1		1	1	1	1	1	1	1.) Monitor plume stability in vicinity of NZ-1; 2.) confirm definition of geochemical zones and arsenic in groundwater; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-121A	Existing	115 River Rd.	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability in vicinity of NZ-3 and adjacent to occupied building; 2.) confirm definition of geochemical zones and arsenic in groundwater.
MW-121B	Existing	115 River Rd.	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability in vicinity of NZ-3; 2.) confirm definition of geochemical zones and arsenic in groundwater.
MW-127	New	Block 93 Central	1	1	1	1	1	1	1		1	1	1	1.) Define the western extent of dissolved-phase organic contamination associated with NZ-4; 2.) define geochemical zones and arsenic in groundwater.
3Y-MW-2	Existing	Block 93 North	1	1	1	1		1	1	1	1	1	1	1.) Monitor plume stability between former acid plant source material and along northern edge of OUI and the MW-111 well series; 2.) confirm definition of geochemical zones and arsenic in groundwater; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-101A	Existing	Block 93 North						1	1		1	1	1	1.) Monitor plume stability upgradient to the west of NZ-1; 2.) confirm definition of geochemical zones and arsenic in groundwater.
MW-111B	Existing	Block 93 North	1	1	1	1		1	1	1	1	1	1	1.) Monitor plume stability along the western edge of OUI; 2.) confirm definition of geochemical zones and arsenic in groundwater; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-123	New	Block 93 South	1	1	1	1	1	1	1		1	1	1	1.) Monitor plume conditions immediately in the vicinity of NZ-4; 2.) define geochemical zones and arsenic in groundwater; and 3.) determine if NAPL observed in TarGOST® boring TL12-10.75 at 12-16 ft. bgs is free-phase (i.e. will accumulate within the well).
MW-124	New	Block 93 South	1	1	1	1	1	1	1		1	1	1	1.) Define the southwestern extent of dissolved-phase organic contamination associated with NZ-4; 2.) define geochemical zones and arsenic in groundwater.
MW-128	New	Block 94	1	1	1	1	1	1	1	1	1	1	1	1.) Define geochemical zones and extent of arsenic west of the MW-111 series wells; 2.) Determine groundwater flow direction between Block 93 and Block 94; 3.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 1; 4.) Define the extent of dissolved-phase organic constituents west of Block 93 North; and 5.) Understand mobility (speciation) of arsenic in groundwater.
MW-129	New	Block 94	1	1	1	1	1	1	1		1	1	1	1.) Define the extent of dissolved-phase organic constituents west of Block 93 North; 2.) Define geochemical zones and extent of arsenic west of the MW-111 series wells; and 3.) Determine groundwater flow direction between Block 93 and Block 94.
MW-133	New	Fmr Celotex			1	1		1	1	1	1	1	1	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 2 downgradient of Geochemical Zone 1A; 2.) Determine whether there is a connection between dissolved As associated with pyritic material observed in the northwest corner of the Quanta property and that observed hydraulically downgradient adjacent to the River at MW-C; 3.) Determine if arsenic observed at MW-C attenuates prior to reaching the shoreline of the River; 4.) Refine the boundaries of Geochemical Zones 4 and 5; and 5.) Determine if NAPL observed at the former Celotex property in NAPL Zone NZ-5 is mobile (i.e. recoverable); and 5.) Understand mobility (speciation) of arsenic in groundwater.
MW-134	New	Fmr Celotex			1	1		1	1	1	1	1	1	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 2 at the boundary between Geochemical Zones 5 and 4; 2.) Determine whether there is a connection between dissolved As associated with pyritic material observed in the northwest corner of the Quanta property and that observed hydraulically downgradient adjacent to the River at MW-C; 3.) Determine if arsenic observed at MW-C attenuates prior to reaching the shoreline of the River; 4.) Refine the boundaries of Geochemical Zones 4 and 5; and 5.) Determine if NAPL observed at the former Celotex property in NAPL Zone NZ-5 is mobile (i.e. recoverable); and 5.) Understand mobility (speciation) of arsenic in groundwater.

TABLE 5  
SUPPLEMENTAL REMEDIAL INVESTIGATION SEMI-ANNUAL  
GROUNDWATER SAMPLING AND ANALYSIS PLAN  
May 2008  
Quanta Resources Superfund Site  
Edgewater, New Jersey

Monitoring Well ID	New or Existing Monitoring Well	Property	Laboratory Analytical Samples - All Semi-Annual Events				Laboratory Analytical Samples - First Semi-Annual Event Only							Data Quality Objective (DQO)
			<sup>2</sup> VOC	<sup>2</sup> SVOC	<sup>5</sup> Dissolved As, Pb, Fe	<sup>5</sup> Total As, Pb, Fe	<sup>2</sup> PCBs	Dissolved TAL Metals (field filtered)	Total TAL Metals (non-filtered)	As III and IV Speciation (non-filtered)	<sup>3</sup> Additional Major Ions (non-filtered)	Alkalinity	Dissolved Organic Carbon	
MW-135	New	Fmr Celotex												1.) Determine if NAPL observed at the former Celotex property in NAPL Zone NZ-5 is mobile (i.e. recoverable) and whether it is connected to NAPL at NZ-2;
MW-106A	Existing	Fmr Lever Bros.	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability proximal to the Hudson River; 2.) confirm definition of geochemical zones and arsenic in groundwater
MW-107A	Existing	Fmr Lever Bros.	1	1	1	1		1	1	1	1	1	1	1.) Monitor plume stability along southern border of OU1 downgradient of NZ-3; 2.) confirm definition of geochemical zones and arsenic in groundwater; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-109	Existing	Fmr Lever Bros.	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability proximal to the Hudson River; 2.) confirm definition of geochemical zones and arsenic in groundwater
MW-115A	Existing	Fmr Lever Bros.	1	1	1	1		1	1	1	1	1	1	1.) Monitor plume stability along southern border of OU1 downgradient of NZ-3; 2.) confirm definition of geochemical zones and arsenic in groundwater; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-115B	Existing	Fmr Lever Bros.	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability along southern border of OU1 downgradient of NZ-3; 2.) confirm definition of geochemical zones and arsenic in groundwater
MW-130A	New	Fmr Lever Bros.	1	1	1	1		1	1	1	1	1	1	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 3 downgradient of Geochemical Zone 3 and whether there is connection between dissolved As observed at the MW-114 series wells and that observed at the MW-107 series wells; 2.) Refine the extent of dissolved-phase organic constituents south of former OU1 operations in shallow unconfined unit (water table); and 3.) Refine the boundaries of Geochemical Zones 3 and 1B; and 4.) Understand mobility (speciation) of arsenic in groundwater.
MW-130B	New	Fmr Lever Bros.	1	1	1	1		1	1	1	1	1	1	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 3 downgradient of Geochemical Zone 3 and whether there is connection between dissolved As observed at the MW-114 series wells and that observed at the MW-107 series wells; 2.) Refine the extent of dissolved-phase organic constituents south of former OU1 operations in deeper unconfined unit (water table); and 3.) Refine the boundaries of Geochemical Zones 3 and 1B; and 4.) Understand mobility (speciation) of arsenic in groundwater.
MW-131	New	Fmr Lever Bros.	1	1	1	1		1	1		1	1	1	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 3 downgradient of Geochemical Zone 1B; 2.) Determine the extent of dissolved-phase organic constituents and arsenic in groundwater hydraulically downgradient of the MW-107 series wells; and 3.) Refine the boundaries of Geochemical Zones 1B, 3 and 5.
MW-132	New	Fmr Lever Bros.	1	1	1	1		1	1	1	1	1	1	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 3 downgradient of Geochemical Zone 1B and immediately upgradient of the River; 2.) Determine the extent of dissolved-phase impacts south of elevated arsenic and coal tar constituents in groundwater hydraulically downgradient of the MW-107 series wells; 3.) Determine if dissolved-phase organic constituents and arsenic are reaching the shoreline of the River; and 4.) Refine the boundaries of Geochemical Zones 4 and 5; and 5.) Understand mobility (speciation) of arsenic in groundwater.
MW-30	Existing	Fmr Lever Bros.	1	1	1	1		1	1		1	1	1	1.) confirm plume definition and stability along south eastern border of OU1 between NZ-3 and the Hudson River at well previously installed and sampled only by GZA; 2.) confirm definition of geochemical zones and arsenic in groundwater
MW-51A	Existing	Fmr Lever Bros.	1	1	1	1		1	1	1	1	1	1	1.) confirm plume definition and stability along south eastern border of OU1 between NZ-3 and the Hudson River at well previously installed and sampled only by GZA; 2.) confirm definition of geochemical zones and arsenic in groundwater; and 3.) Understand mobility (speciation) of arsenic in groundwater.
ACMW-3	Existing	Fmr. Celotex						1	1		1	1	1	1.) Monitor plume stability downgradient to the northeast of OU1 and the former acid plant source material; 2.) confirm definition of geochemical zones and arsenic in groundwater

TABLE 5  
SUPPLEMENTAL REMEDIAL INVESTIGATION SEMI-ANNUAL  
GROUNDWATER SAMPLING AND ANALYSIS PLAN  
May 2008  
Quanta Resources Superfund Site  
Edgewater, New Jersey

Monitoring Well ID	New or Existing Monitoring Well	Property	Laboratory Analytical Samples - All Semi-Annual Events				Laboratory Analytical Samples - First Semi-Annual Event Only							Data Quality Objective (DQO)
			<sup>1</sup> VOC	<sup>2</sup> SVOC	<sup>5</sup> Dissolved As, Pb, Fe	<sup>5</sup> Total As, Pb, Fe	<sup>2</sup> PCBs	Dissolved TAL Metals (field filtered)	Total TAL Metals (non-filtered)	As III and IV Speciation (non-filtered)	<sup>3</sup> Additional Major Ions (non-filtered)	Alkalinity	Dissolved Organic Carbon	
MW-20	Existing	Fmr. Celotex	1	1	1	1		1	1	1	1	1	1	1.) Monitor plume stability downgradient of former acid plant source material and along northern edge of OU1; 2.) confirm definition of geochemical zones and arsenic in groundwater; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-A-1	Existing	Fmr. Celotex						1	1		1	1	1	1.) confirm definition of geochemical zones and arsenic in groundwater
MW-A-2	Existing	- Fmr. Celotex	1	1	1	1		1	1	1	1	1	1	1.) confirm definition of geochemical zones and arsenic in groundwater; and 2.) refine dissolved-phase organic contaminant distribution northwest of the Quanta property; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-B	Existing	Fmr. Celotex	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability downgradient of former acid plant source material and along northern edge of OU1; 2.) confirm definition of geochemical zones and arsenic in groundwater
MW-C	Existing	Fmr. Celotex	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability proximal to the Hudson River in vicinity of NZ-2; 2.) confirm definition of geochemical zones in groundwater
MW-F	Existing	Fmr. Celotex	1	1	1	1		1	1	1	1	1	1	1.) Monitor plume stability proximal to the Hudson River in vicinity of NZ-2; 2.) confirm definition of geochemical zones and arsenic in groundwater; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-N-1	Existing	Fmr. Celotex						1	1		1	1	1	1.) confirm definition of geochemical zones and arsenic in groundwater
MW-N-2	Existing	Fmr. Celotex	1	1	1	1		1	1	1	1	1	1	1.) confirm definition of geochemical zones and arsenic in groundwater; 2.) refine dissolved-phase organic contaminant distribution northwest of the Quanta property; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-O	Existing	Fmr. Celotex	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability proximal to the Hudson River in vicinity of NZ-2; 2.) confirm definition of geochemical zones in groundwater
MW-L	Existing	Gorge Rd.	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability upgradient to the northwest of OU1 and the former acid plant source material; 2.) confirm definition of geochemical zones and arsenic in groundwater
MW-125	New	Gorge/Old River Rd	1	1	1	1	1	1	1		1	1	1	1.) Define the extent of dissolved-phase organic constituents on the upgradient edge of former OU1 operations; and 2.) Define geochemical zones and extent of arsenic northwest of the MW-111 series wells
MW-126	New	Gorge/River Rd	1	1	1	1	1	1	1	1	1	1	1	1.) Correlate results of SEP analyses with groundwater results to determine arsenic mobility along Transect 1, hydraulically downgradient the pyritic waste material and along the boundary between Geochemical zones 1A and 2; 2.) Determine whether there is connection between dissolved As associated with pyritic material (MW-N series wells) and that observed at the MW-111 series wells; 3.) Refine the boundaries of Geochemical Zones 2 and 5; 4.) Refine the extent of dissolved-phase organic constituents within the intersection of Gorge and River Roads (near former ASTs); 5.) Confirm the direction of groundwater flow between the pyritic waste material and Block 93 North; and 6.) Understand mobility (speciation) of arsenic in groundwater.
MW-103A	Existing	Quanta	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability in vicinity of NZ-3; 2.) confirm definition of geochemical zones and arsenic in groundwater
MW-105A	Existing	Quanta	1	1	1	1		1	1	1	1	1	1	1.) Monitor plume stability proximal to the Hudson River in vicinity of NZ-2; 2.) confirm definition of geochemical zones and arsenic in groundwater; and 3.) Understand mobility (speciation) of arsenic in groundwater.
MW-112A	Existing	Quanta						1	1		1	1	1	1.) confirm definition of geochemical zones and arsenic in groundwater
MW-112B	Existing	Quanta						1	1		1	1	1	1.) confirm definition of geochemical zones and arsenic in groundwater
MW-113A	Existing	Quanta						1	1		1	1	1	1.) confirm definition of geochemical zones and arsenic in groundwater

TABLE 5  
SUPPLEMENTAL REMEDIAL INVESTIGATION SEMI-ANNUAL  
GROUNDWATER SAMPLING AND ANALYSIS PLAN  
May 2008  
Quanta Resources Superfund Site  
Edgewater, New Jersey

Monitoring Well ID	New or Existing Monitoring Well	Property	1Laboratory Analytical Samples - All Semi-Annual Events				1Laboratory Analytical Samples - First Semi-Annual Event Only						Data Quality Objective (DQO)	
			2VOC	2SVOC	5Dissolved As, Pb, Fe	5Total As, Pb, Fe	2PCBs	Dissolved TAL Metals (field filtered)	Total TAL Metals (non-filtered)	As III and IV Speciation (non-filtered)	3Additional Major Ions (non-filtered)	Alkalinity		Dissolved Organic Carbon
MW-113B	Existing	Quanta	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability immediately downgradient of former acid plant source material and NZ-1; 2.) confirm definition of geochemical zones and arsenic in groundwater
MW-113C	Existing	Quanta						1	1		1	1	1	1.) confirm definition of geochemical zones and arsenic in groundwater
MW-117B	Existing	Quanta	1	1	1	1		1	1		1	1	1	1.) Monitor plume stability proximal to the Hudson River in vicinity of NZ-2; 2.) confirm definition of geochemical zones and arsenic in groundwater

**Notes:**

1. Specific laboratory analytical methods and analyte lists are provided in the revised Quality Assurance Project Plan (QAPP) (CH2M Hill, 2005; 2006a) or in Attachment A of this Work Plan Addendum. QA/QC Samples will be taken at the frequency specified in the revised QAPP (CH2M Hill, 2005; 2006a) (Both MS/MSD and Field Duplicates = 1 per 20 samples (5% per matrix).
2. VOCs: volatile organic compounds, SVOCs: semi-volatile organic compounds, TAL Metals (Target Analyte Metals), PCBs: polychlorinated biphenyls
3. Groundwater grab sample location will be collected during completion of the soil boring at this location (in advance of the first semi-annual event).
4. Newly installed monitoring wells will be sampled as part of the proposed semi-annual sampling event. Analyses performed on newly installed monitoring will include PCBs during the first event only unless detections are observed.
5. Additional Major Ions (not included in TAL Metals analysis): sulfate, sulfide, nitrate, and chloride
6. The need to sample this well beyond the 1st Proposed Semi-Annual Groundwater Sampling Event will be evaluated upon receipt of analytical results from the initial sampling event.
7. During the 1st Proposed Semi-Annual Groundwater Sampling Event all samples will be analyzed for Dissolved TAL Metals and will include these parameters.

**TABLE 6**  
**SUPPLEMENTAL REMEDIAL INVESTIGATION**  
**SHORELINE AND WOODEN BULKHEAD CHARACTERIZATION**  
 May 2008  
 Quanta Resources Superfund Site  
 Edgewater, New Jersey

Property	<sup>1</sup> Proposed Location/ Boring ID	Method	Data Collection Activities and Installations				<sup>4</sup> Data Quality Objectives (DQO)
			Continuous Sampling	Borehole Geophysics	Nested Piezometers	Monitoring Well	
Quanta	PZ-6	Sonic	X	X	X		1.) Determine vertical extent of NAPL behind bulkhead and potential just upgradient of the northern end of the bulkhead; 2.) Confirm the presence or absence of the bulkhead along the northeastern edge of the Quanta property and determine it's depth at this location; 3.) Allow installation of nested piezometers for purpose of GSI Evaluation.
Quanta	PZ-7	Sonic	X	X	X		1.) Determine vertical extent of NAPL directly behind bulkhead; 2.) Determine the vertical extent of the bulkhead where it is known to be present; 3.) Allow installation of nested piezometers for purpose of GSI Evaluation.
Quanta	PZ-8	Sonic	X	X	X		1.) Determine vertical extent of NAPL directly behind bulkhead and potential just upgradient of the southern end of the bulkhead; 2.) Confirm the presence or absence of the bulkhead along the southeastern edge of the Quanta property and determine it's depth at this location; 3.) Allow installation of nested piezometers for purpose of GSI Evaluation.
Quanta	BH-1	Sonic	X				1.) Determine vertical extent of NAPL directly behind bulkhead; 2.) Determine the vertical extent of the bulkhead where it is known to be present.
Quanta	BH-2	Sonic	X				1.) Determine vertical extent of NAPL directly behind bulkhead; 2.) Determine the vertical extent of the bulkhead where it is known to be present.
Quanta	BH-3	Sonic	X				1.) Determine vertical extent of NAPL directly behind bulkhead; 2.) Confirm the presence or absence of the bulkhead along the southeastern edge of the Quanta property and determine it's depth at this location.
Former Celotex	MW-135	Sonic	X	X		X	1.) Determine if NAPL observed at the former Celotex property in NAPL Zone NZ-5 is mobile (i.e. recoverable) and whether it is connected to NAPL at NZ-2 (i.e. NAPL behind the bulkhead).

**Notes:**

1. Exact locations and depths of PZ-6 through 8 will be determined following the analysis of the Phase 1 geophysical investigations in order to assure borehole depths that exceed the depth of the bulkhead and to allow for piezometer installations just beyond the lateral extents of the wooden bulkhead.
2. GSI: Groundwater Surface Water Interaction

TABLE 7  
SUPPLEMENTAL REMEDIAL INVESTIGATION  
GROUNDWATER/ SURFACE WATER INVESTIGATION SAMPLING AND ANALYSIS PLAN  
May 2008  
Quanta Resources Superfund Site  
Edgewater, New Jersey

Location ID	Location	Piezometer Installed & Hydraulic Head Measurements	Install Method	Construction Diameter (inches) and Type	Anticipated Screen Interval (ft. bgs)	<sup>2</sup> Pore Water Laboratory Analytical Samples					<sup>2</sup> Surface Water Laboratory Analytical Samples				Data Quality Objective (DQO)
						VOC	SVOC	Dissolved As (field-filtered)	Total As (non-filtered)	As III and IV Speciation	VOC	SVOC	Dissolved As (field-filtered)	Total As (non-filtered)	
GWZ-1	OU2 (TBD)		N/A	N/A	N/A	1	1	1	1	1	1	1	1	1	1.) Determine the distribution of coal tar constituents and arsenic in shallow pore water; 2.) enhance conceptual model of coal tar constituent and arsenic fate and transport from OU1 groundwater; and 3.) Quantify risk to potential ecological receptors within the biologically active zone in sediment.
GWZ-2	OU2 (TBD)		N/A	N/A	N/A	1	1	1	1	1	1	1	1	1	
GWZ-3	OU2 (TBD)		N/A	N/A	N/A	1	1	1	1	1	1	1	1	1	
GWZ-4	OU2 (TBD)		N/A	N/A	N/A	1	1	1	1	1	1	1	1	1	
GWZ-5	OU2 (TBD)		N/A	N/A	N/A	1	1	1	1	1	1	1	1	1	
PZ-1S	OU2	X	Hand-driven	1/2-inch SS	4.5-5	1	1	1	1						1.) Gain an understanding of groundwater flow paths between observed contamination at OU1 and groundwater discharge areas at OU2; 2.) Determine the distribution of coal tar constituents and arsenic in pore water at varying depths between OU1 and OU2
PZ-1I			Hand-driven	1/2-inch SS	14.5-15	1	1	1	1						
PZ-1D			Hand-driven	1/2-inch SS	24.5-25	1	1	1	1						
PZ-2S	OU2	X	Hand-driven	1/2-inch SS	4.5-5	1	1	1	1						
PZ-2I			Hand-driven	1/2-inch SS	14.5-15	1	1	1	1						
PZ-2D			Hand-driven	1/2-inch SS	24.5-25	1	1	1	1						
PZ-3S	OU2	X	Hand-driven	1/2-inch SS	4.5-5	1	1	1	1						
PZ-3I			Hand-driven	1/2-inch SS	14.5-15	1	1	1	1						
PZ-3D			Hand-driven	1/2-inch SS	24.5-25	1	1	1	1						
PZ-4S	OU2	X	Hand-driven	1/2-inch SS	4.5-5	1	1	1	1						
PZ-4I			Hand-driven	1/2-inch SS	14.5-15	1	1	1	1						
PZ-4D			Hand-driven	1/2-inch SS	24.5-25	1	1	1	1						
PZ-5S	OU2	X	Hand-driven	1/2-inch SS	4.5-5	1	1	1	1						1.) Gain an understanding of groundwater flow paths between observed contamination at OU1 and groundwater discharge areas at OU2; 2.) Evaluate the role of the bulkhead as a hydraulic barrier and a barrier to NAPL and dissolved phase constituent migration from OU1 to OU2.
PZ-5I			Hand-driven	1/2-inch SS	14.5-15	1	1	1	1						
PZ-5D			Hand-driven	1/2-inch SS	24.5-25	1	1	1	1						
PZ-6S	OU1	X	Sonic	1-inch PVC	10-12										
PZ-6I				1-inch PVC	23-25										
PZ-6D				2-inch PVC	33-35										
PZ-7S	OU1	X	Sonic	1-inch PVC	10-12										
PZ-7I				1-inch PVC	23-25										
PZ-7D				2-inch PVC	33-35										
PZ-8S	OU1	X	Sonic	1-inch PVC	10-12										
PZ-8I				1-inch PVC	23-25										
PZ-8D				2-inch PVC	33-35										

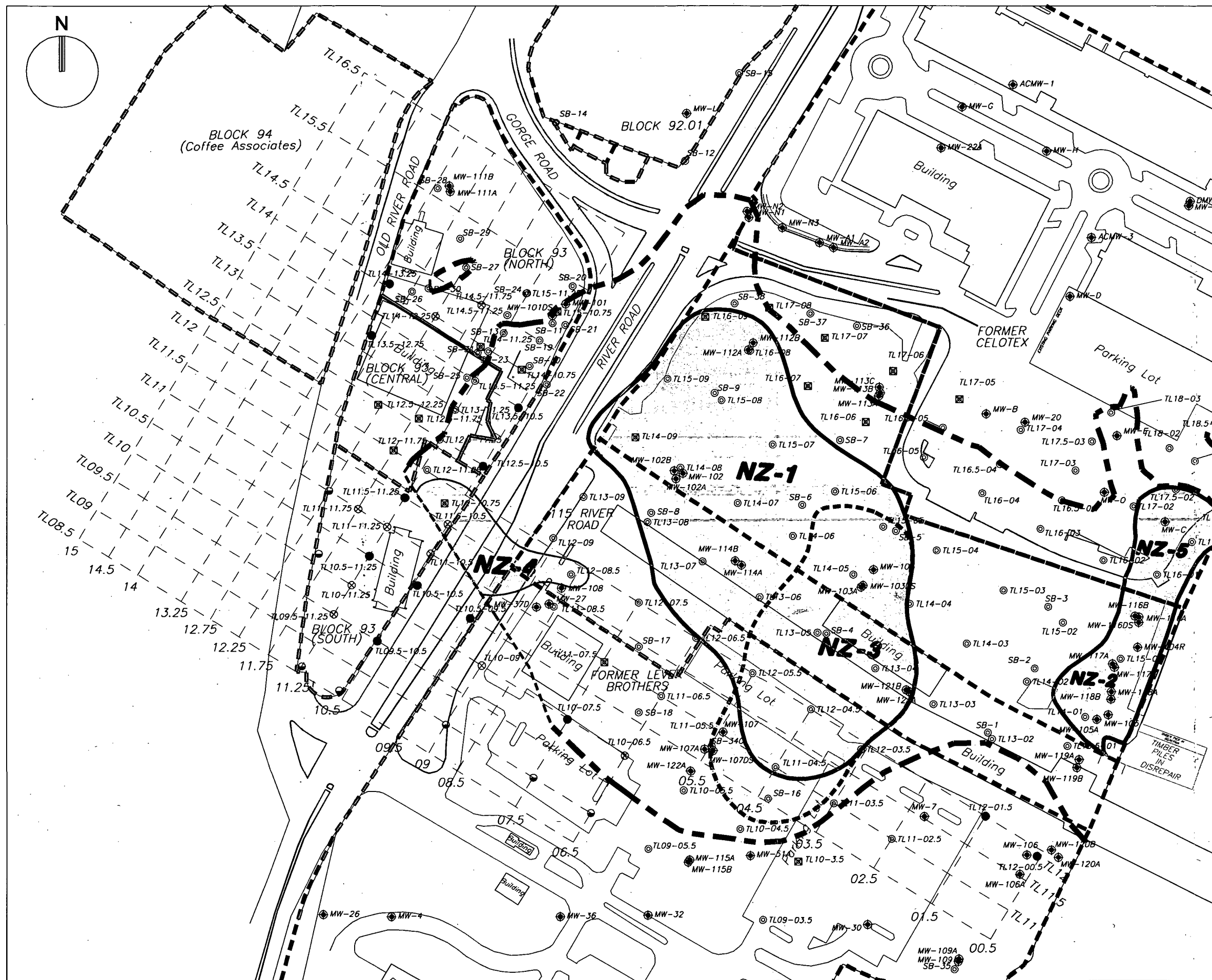
**Notes:**

- Locations GWZ-1 through GWZ-5 will be selected based on the results of the Trident Probe Survey and will target areas of preferential groundwater discharge at OU2. Exact locations and depths of PZ-6 through 8 will be determined following the analysis of the Phase 1 geophysical investigations in order to assure borehole depths that exceed the depth of the bulkhead and to allow for piezometer installations just beyond the lateral extents of the wooden bulkhead.
- Specific laboratory analytical methods and analyte lists are provided in the revised Quality Assurance Project Plan (QAPP) (CH2M Hill, 2005; 2006a) or in Attachment A of this Work Plan Addendum. QA/QC Samples will be taken at the frequency specified in the revised QAPP (CH2M Hill, 2005; 2006a) (Both MS/MSD and Field Duplicates = 1 per 20 samples (5%) per matrix).
- VOCs: volatile organic compounds, SVOCs: semi-volatile organic compounds, As (arsenic)

## Figures

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## LEGEND

- TL10 + — TarGOST™ GRID LINES
- ⊗ PROPOSED TarGOST® LOCATION
- PROPOSED TarGOST® & SOIL DIRECT-PUSH SOIL SAMPLING & ANALYSIS LOCATION
- ◉ CONTINGENCY TarGOST® LOCATION
- ⊙ EXISTING SOIL BORING
- ⊠ EXISTING TarGOST® BORING WITH ANALYTICAL DATA
- ⊕ EXISTING MONITORING WELL
- EXTENT OF NON-AQUEOUS PHASE LIQUID (NAPL) (DOTTED WHERE INFERRED)
- ⊠ KEY NAPL ZONES
- CURRENT PROPERTY BOUNDARY

### NOTES:

1. All data points defining the extent of non-aqueous phase liquid (NAPL) that were collected as part of investigations other than the OU1 RI/FS are not necessarily depicted due to the density of data.
2. Depiction of other properties are based on available tax maps and drawings generated by other consultants as part of environmental studies.
3. Depiction of other properties on this figure is for comparative purposes and does not necessarily suggest that site-related constituents have migrated there.

### GRAPHIC SCALE



## SRI - PROPOSED TarGOST® INVESTIGATION LOCATIONS

Quanta Resources Superfund Site  
Edgewater, New Jersey

May 14, 2008

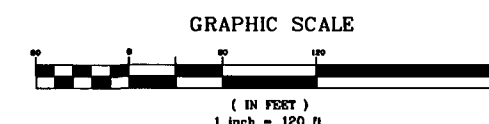
FIGURE 1



# LEGEND

- TarGOST® GRID LINES
- PROPOSED ROTASONIC BORING & SOIL SAMPLING LOCATION WHERE MONITORING WELL WILL BE INSTALLED
- PROPOSED DIRECT-PUSH BORING & SOIL SAMPLING LOCATION
- PROPOSED DIRECT-PUSH BORING AND SOIL SAMPLING LOCATION COLLOCATED w/TarGOST®
- PROPOSED DIRECT-PUSH BORING & SOIL SAMPLING LOCATION W/GROUNDWATER GRAB
- EXISTING SOIL BORING
- EXISTING TarGOST® BORING WITH ANALYTICAL DATA
- EXISTING MONITORING WELL
- LATERAL EXTENT OF COAL TAR BASED ON TarGOST®, SOIL BORING AND MONITORING WELL OBSERVATIONS. INCLUDES STAINED AND ODOROUS SOILS WHERE NAPL WAS NOT OBSERVED (DASHED WHERE ADDITIONAL DELINEATION NEEDED)
- CURRENT PROPERTY BOUNDARY

- NOTES:**
1. All data points defining the lateral extent of coal tar as defined above that were collected as part of investigations other than the OU1 RI/FS are not necessarily depicted due to the density of data.
  2. Depiction of other properties are based on available tax maps and drawings generated by other consultants as part of environmental studies.
  3. Depiction of other properties on this figure is for comparative purposes and does not necessarily suggest that site-related constituents have migrated there.



**SRI - PROPOSED ORGANIC  
CONSTITUENT SOIL  
SAMPLING LOCATIONS**

**Quanta Resources Superfund Site  
Edgewater, New Jersey**

May 14, 2008

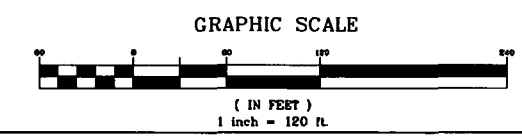
**FIGURE 2**



# LEGEND

- MW-126 PROPOSED ROTASONIC BORING & SOIL SAMPLING LOCATION WHERE MONITORING WELL WILL BE INSTALLED
- SB-49 PROPOSED DIRECT-PUSH BORING & SOIL SAMPLING LOCATION
- TWP-SB-41 PROPOSED DIRECT-PUSH BORING & SOIL SAMPLING LOCATION W/GROUNDWATER GRAB
- TL10-07.5 PROPOSED DIRECT-PUSH BORING AND SOIL SAMPLING LOCATION COLOCATED w/TarGOST®
- EXISTING SOIL BORING
- EXISTING TarGOST® BORING WITH ANALYTICAL DATA
- EXISTING MONITORING WELL
- LATERAL EXTENT OF ARSENIC IN SOIL GREATER THAN 100 MG/KG
- CURRENT PROPERTY BOUNDARY

NOTES:  
 1. All data points defining isoconcentration contours that were collected as part of investigations other than the OU1 RI/FS are not necessarily depicted due to the density of data.  
 2. Depiction of other properties are based on available tax maps and drawings generated by other consultants as part of environmental studies.  
 3. Depiction of other properties on this figure is for comparative purposes and does not necessarily suggest that site-related constituents have migrated there.



SRI - PROPOSED METALS SOIL SAMPLING LOCATIONS

Quanta Resources Superfund Site  
 Edgewater, New Jersey

May 14, 2008

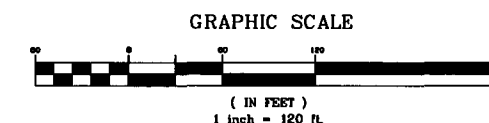
FIGURE 3



## LEGEND

- MW-126 PROPOSED ROTASONIC BORING & SOIL SAMPLING LOCATION WHERE MONITORING WELL WILL BE INSTALLED
- SB-49 PROPOSED DIRECT-PUSH OR ROTASONIC BORING & SOIL SAMPLING LOCATION
- EXISTING SOIL BORING
- EXISTING TarGOST® BORING WITH ANALYTICAL DATA
- EXISTING MONITORING WELL
- 100 — ARSENIC ISOCONCENTRATION CONTOUR IN GROUNDWATER
- CURRENT PROPERTY BOUNDARY

**NOTES:**  
1. All data points defining isoconcentration contours that were collected as part of investigations other than the OU1 RI/FS are not necessarily depicted due to the density of data.  
2. Depiction of other properties are based on available tax maps and drawings generated by other consultants as part of environmental studies.  
3. Depiction of other properties on this figure is for comparative purposes and does not necessarily suggest that site-related constituents have migrated there.



**SRI - PROPOSED ARSENIC SEQUENTIAL EXTRACTION PROCESS (SEP) SOIL SAMPLING LOCATIONS**

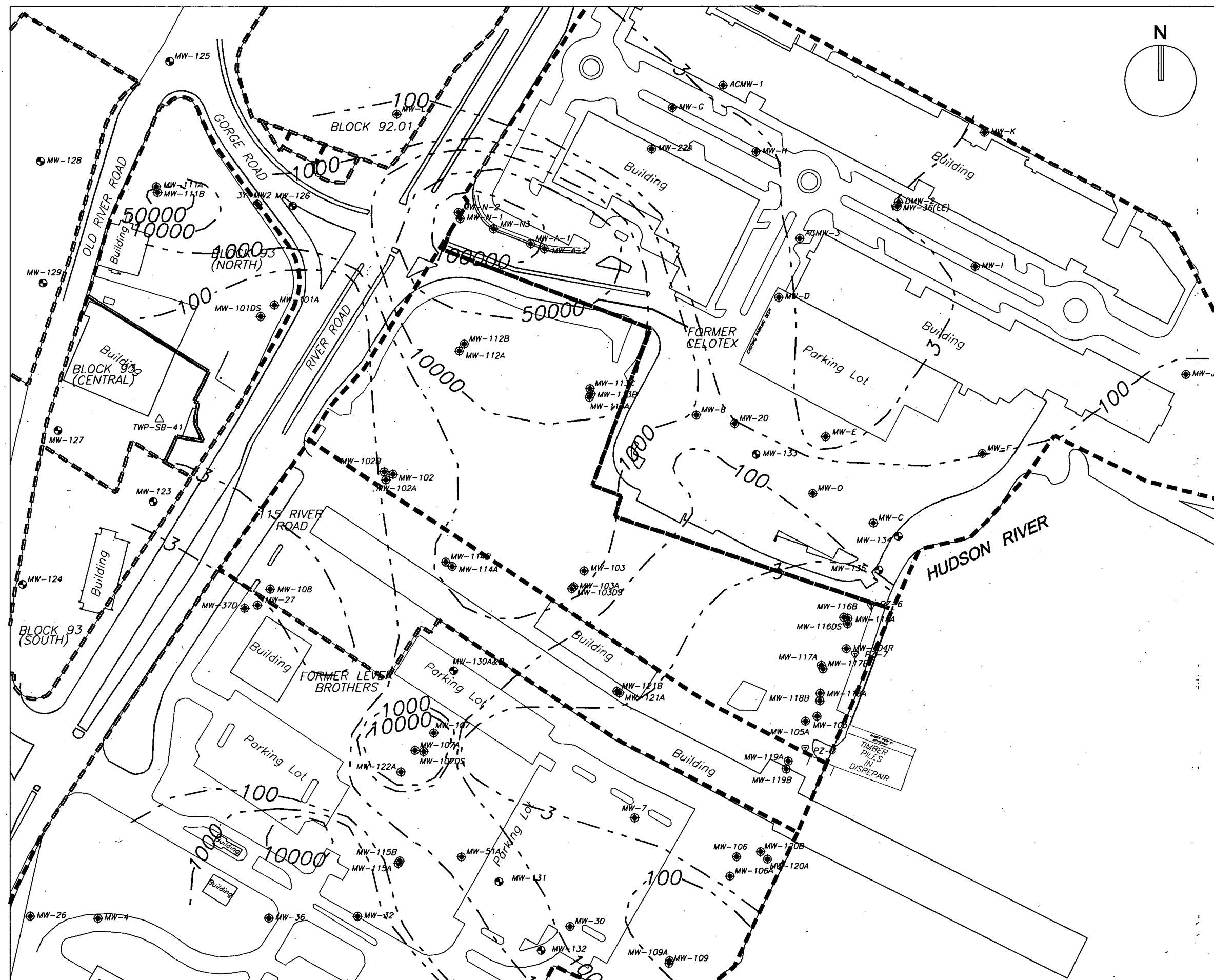
**Quanta Resources Superfund Site  
Edgewater, New Jersey**

May 14, 2008









**FIGURE 4**







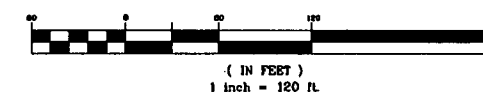
## LEGEND

-  NEWLY INSTALLED MONITORING WELLS
-  EXISTING MONITORING WELLS
-  PROPOSED LOCATION FOR BOTH 2008 SEMI-ANNUAL GROUNDWATER SAMPLING EVENTS (INCLUDES GEOCHEMICAL PARAMETERS FOR 1ST EVENT ONLY)
-  PROPOSED LOCATION FOR BOTH 2008 SEMI-ANNUAL GROUNDWATER SAMPLING EVENTS (INCLUDES ARSENIC III AND V SPECIATION AND GEOCHEMICAL PARAMETERS FOR 1ST EVENT ONLY)
-  GROUNDWATER SAMPLING LOCATION FOR 1ST 2008 SEMI-ANNUAL SAMPLING EVENT ONLY (INCLUDES GEOCHEMICAL PARAMETERS)
-  PROPOSED ONE-TIME GROUNDWATER GRAB SAMPLING LOCATION (NO GEOCHEMICAL PARAMETERS)
-  LOCATION FOR FOR GAUGING ONLY
- 100 — ARSENIC ISOCONCENTRATION CONTOUR IN GROUNDWATER
-  CURRENT PROPERTY BOUNDARY

**NOTES:**

1. All data points defining Isoconcentration contours that were collected as part of investigations other than the OU1 RI/FS are not necessarily depicted due to the density of data.
2. Depiction of other properties are based on available tax maps and drawings generated by other consultants as part of environmental studies.
3. Depiction of other properties on this figure is for comparative purposes and does not necessarily suggest that site-related constituents have migrated there.

GRAPHIC SCALE

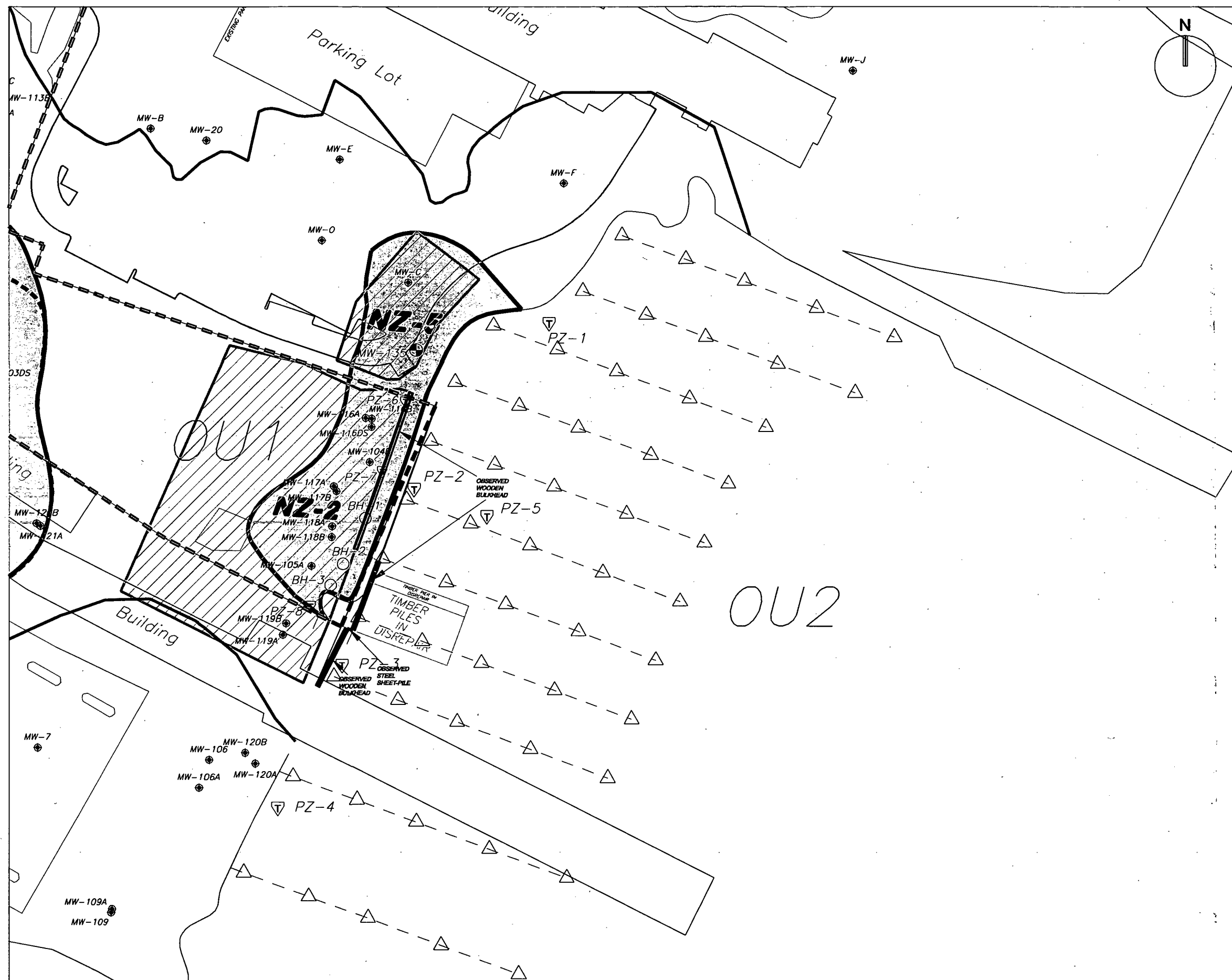
**CH2MHILL**

**SRI - PROPOSED METALS & GEOCHEMICAL  
GROUNDWATER SAMPLING LOCATIONS**

**Quanta Resources Superfund Site  
Edgewater, New Jersey**

May 14, 2008

**FIGURE 6**

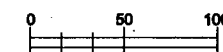


## LEGEND

- QUANTA PROPERTY BOUNDARY
- HUDSON RIVER SHORELINE
- EXTENT OF COAL TAR (INCLUDES NON-AQUEOUS PHASE LIQUID (NAPL), SOLID TARS, AND SOIL IMPACTS)
- NZ-2** KEY NAPL ZONE
- EXISTING GROUNDWATER MONITORING WELL
- △ PROPOSED TRIDENT PROBE LOCATION
- ▽ PROPOSED HAND-DRIVEN NESTED PIEZOMETER - OU2
- ▽ PROPOSED DRILLED NESTED PIEZOMETER - OU1
- PROPOSED BOREHOLE GEOPHYSICS LOCATION
- PROPOSED SHORELINE ROTASONIC BORING
- ▨ APPROXIMATE AREA OF PROPOSED SURFACE GEOPHYSICS

### Basemap Sources:

- a.) Boundary and topographic survey of Block 85, Lot 1 and Block 83, Lots 1, 2, and 3 performed by Vargo Associates in September 2005 and updated as recently as June 2007.
- b.) Borough of Edgewater Tax Map - November, 1959
- c.) Coal Tar Engineering Design Report (Environ, July 2005)
- d.) Site Investigation Report, Part 4 (Langan, May 2004) for the former Lever Bros. Property.



**CH2MHILL**

**SRI - SHORELINE/ BULKHEAD  
CHARACTERIZATION AND GSI  
EVALUATION LOCATIONS**

**Quanta Resources Superfund Site  
Operable Unit 1  
Edgewater, New Jersey**

May 14, 2008

**FIGURE 7**

Attachment A

**Quality Assurance Project Plan Addendum**



Inorganic arsenic speciation analysis will be conducted for arsenic (III) and arsenic (V) by IC-ICP-MS. Organic arsenic speciation (DMA/MMA) will not be conducted for this sampling event. Prior to analyzing any samples, the instrument(s) must be properly calibrated in accordance with the method and all QA/QC procedure. Soils will also undergo a sequential extraction procedure (SEP) and analysis to determine at what stage arsenic moves from the solid phase to the aqueous phase. Applied Speciation Laboratories of Tulwill, Washington will be conducting the arsenic speciation and SEP. They have current New Jersey Department of Environmental Protection (NJDEP) certification for arsenic speciation analysis.

The following tables serve to update the existing Quality Assurance Project Plan (QAPP) (CH2M HILL, 2005; 2006a) to incorporate the necessary information for additional laboratory analytical methods proposed as part of the OU1 RI/FS Work Plan Addendum No. 4.

**Table 1**

**Additional Required Analytical Method, Sample Containers, Preservation, and Holding Times**

**Quanta Resources OU1, Edgewater, NJ**

Analyses	Analytical Method	Sample Matrix	Container	Qty	Preservative	Holding Time
Metals (Total)	SW-846 SW6010B /6020	W	500-mL polyethylene	1	HNO <sub>3</sub> , pH < 2, Cool 4°C	6 months
	SW-846 SW6010B /6020	S	8-oz glass	1	Cool 4°C	
Metals (Dissolved)	SW-846 SW6010B /6020	W	500-mL polyethylene	1	HNO <sub>3</sub> , pH < 2, Cool 4°C (must be field filtered before acid preserved. If lab filtered, should be preserved at lab)	6 months
Arsenic Speciation As(III) & As(V)	IC-ICP-MS	W	125mL HDPE	1	EDTA, Cool 4°C, keep dark	14 days
Arsenic Sequential Extraction	Sequential Extraction	S	4oz Poly Jar / Intact Core is preferred	1	Cool 4°C	7 days
Total Organic Carbon	SW-846 9060	W	250-mL polyethylene	1	H <sub>2</sub> SO <sub>4</sub> or HCl pH < 2, Cool 4°C	28 days
		S	4-oz glass	1	Cool 4°C	28 days
Dissolved Organic Carbon	SW-846 9060	W	250-mL polyethylene	1	H <sub>2</sub> SO <sub>4</sub> or HCl pH < 2, Cool 4°C	28 days
Sulfate	EPA 300.0	W	250-mL polyethylene	1	Cool 4°C	28 days
		S	8-oz glass	1		

Table 1

## Additional Required Analytical Method, Sample Containers, Preservation, and Holding Times

Quanta Resources OU1, Edgewater, NJ

Analyses	Analytical Method	Sample Matrix	Container	Qty	Preservative	Holding Time
Sulfide	EPA 300.0	W	500-mL polyethylene	1	Cool 4°C; NaOH, Zinc Acetate	7 days
Nitrate	EPA 300.0	W	250-mL polyethylene 8-oz glass	1	Cool 4°C	48 hours
		S		1		
Chloride	EPA 300.0	W	250-mL polyethylene 8-oz glass	1	Cool 4°C	28 days
		S		1		
Alkalinity	SM2320B	W	500-mL polyethylene	1	Cool 4°C	14 days

## Notes:

Sample container, and volume requirements will be specified by the analytical laboratory performing the tests.

Three times the required volume should be collected for samples designated as MS/MSD samples.

<sup>a</sup>Sample matrix: S = surface soil, subsurface soil, sediment; W = surface water<sup>b</sup>All containers will be sealed with Teflon®-lined screw caps.<sup>c</sup>All samples will be stored promptly at 4°C in an insulated chest.<sup>d</sup>Holding times are from the time of sample collection.<sup>e</sup>14 days to TCLP extraction, 7 days for extraction, 40 days for analysis<sup>f</sup>7 days to extraction for water, 40 days for analysis.<sup>g</sup>14 days to extraction for soil, 40 days for analysis.<sup>h</sup>14 days to TCLP extraction for soil, 40 days for analysis<sup>i</sup>30 days to extraction for water, 45 days for analysis.

Source: SW-846, third edition, Update III (June 1997).

°C = Degrees Centigrade

HCl = Hydrochloric acid

TCLP = Toxicity characteristic leaching procedure

mL = Milliliter

g = Gram

L = Liter

oz = Ounce

EDTA = ethylenediaminetetraacetic acid

TPH = Total petroleum hydrocarbon

NaOH = Sodium hydroxide

HNO<sub>3</sub> = Nitric acid

EPA = U.S. Environmental Protection Agency

H<sub>2</sub>SO<sub>4</sub> = Sulfuric acid

ASTM = American Society for Testing and Materials

NA = Not applicable

**Table 2**

**Quality Control Limits for Arsenic Speciation in Water & Soil**

**Quanta Resources OU1, Edgewater, NJ**

Analyte	MS (% Rec)	Duplicate (% RPD)
Arsenic (III)	70-130	< 20
Arsenic (V)	70-130	< 20

**Table 3**

**Reporting Limits for Arsenic Speciation in Water**

**Quanta Resources OU1, Edgewater, NJ**

Analyte	Reporting Limit (ug/L)	Reporting Limit (ug/Kg)
Arsenic (III)	2.0	20.0
Arsenic (V)	2.0	20.0

**Table 4**

**Quality Control Limits for Metals in Water (Total & Dissolved)  
and Sediments, Methods 6010B, 7470A, 7471A**

**Quanta Resources OU1, Edgewater, NJ**

<b>Analyte</b>	<b>MS (% Rec)</b>	<b>Duplicate (% RPD)</b>	<b>Blank Spike (% Rec)</b>
All Analytes	75-125	< 20	80-120%
Aluminum			for all
Antimony			analytes
Arsenic			
Barium			
Beryllium			
Cadmium			
Calcium			
Chromium			
Cobalt			
Copper			
Iron			
Lead			
Magnesium			
Manganese			
Mercury			
Nickel			
Potassium			
Selenium			
Silver			
Sodium			
Thallium			
Vanadium			
Zinc			

Table 5

## Metals Target Analyte List and Reporting Limits in Water (Total &amp; Dissolved)

Quanta Resources OU1, Edgewater, NJ

Analyte	CAS Number	Reporting Limit (mg/l)	Method Detection Limit (ug/l)	NJ Groundwater Criteria (mg/l)
Aluminum	7429-90-5	200	107	200
Antimony	7440-36-0	6.0	4.4	6
Arsenic	7440-38-2	2.0	0.7	3
Barium	7440-39-3	5.0	2.5	2000
Beryllium	7440-41-7	1.0	1.5	1
Cadmium	7440-43-9	4.0	0.6	4
Calcium	7440-70-2	200	62	NA
Chromium	7440-47-3	15	1.6	70
Cobalt	7440-48-4	5.0	1.7	NA
Copper	7440-50-8	10	2.3	1300
Iron	7439-89-6	200	67	300
Lead	7439-92-1	3.0	2.6	5
Magnesium	7439-95-4	100	16	NA
Manganese	7439-96-5	5.0	0.4	50
Mercury	7439-97-6	0.2	0.15	2
Nickel	7440-02-0	10	1.6	100
Potassium	7440-09-7	500	65	NA
Selenium	7782-49-2	10.0	3.0	40
Silver	7440-22-4	5.0	1.9	40
Sodium	7440-23-5	1000	308	50000
Thallium	7440-28-0	2.0	1.2	2
Vanadium	7440-62-2	5.0	1.9	NA
Zinc	7440-66-6	20	3.3	2000

Table 6

## Metals Target Analyte List and Reporting Limits in Soils

Quanta Resources OU1, Edgewater, NJ

Analyte	CAS Number	Reporting Limit (mg/kg)	Method Detection Limit (mg/kg)	NJ Residential Soil Criteria (mg/kg)
Aluminum	7429-90-5	20	4.8	NA
Antimony	7440-36-0	2.0	0.76	14
Arsenic	7440-38-2	2.0	0.76	20
Barium	7440-39-3	5.0	0.3	700
Beryllium	7440-41-7	0.50	0.02	2
Cadmium	7440-43-9	0.50	0.1	39
Calcium	7440-70-2	20	8.9	NA
Chromium	7440-47-3	1.5	0.44	NA
Cobalt	7440-48-4	0.5	0.18	NA
Copper	7440-50-8	1.0	0.23	600
Iron	7439-89-6	20	7.5	NA
Lead	7439-92-1	2.0	0.32	400
Magnesium	7439-95-4	10	1.4	NA
Manganese	7439-96-5	0.5	0.1	NA
Mercury	7439-97-6	0.1	0.024	14
Nickel	7440-02-0	1.0	0.32	250
Potassium	7440-09-7	50	9.0	NA
Selenium	7782-49-2	2.0	0.79	63
Silver	7440-22-4	0.5	0.22	110
Sodium	7440-23-5	100	34	NA
Thallium	7440-28-0	1.0	0.86	2
Vanadium	7440-62-2	0.5	0.1	370
Zinc	7440-66-6	2.0	0.29	1500

**TABLE 7****General Chemistry Analytical Parameter Detection Limits****Quanta Resources OU1, Edgewater, NJ**

<b>Analytical Parameter</b>	<b>Aqueous Method Reporting Limit</b>	<b>Solid Method Reporting Limit</b>
Alkalinity	5.0 mg/L	NA
Chloride	1.0 mg/L	10 mg/kg
Nitrate	1.0 mg/L	10 mg/kg
Sulfate	1.0 mg/L	10 mg/kg
Sulfide	1.0 mg/L	NA
Total Organic Carbon (TOC) / Dissolved Organic Carbon (DOC)	1.0 mg/L	10 mg/kg

**Table 8****Quality Control Limits for General Chemistry Parameters in Water and Sediments****Quanta Resources OU1, Edgewater, NJ**

<b>Analyte</b>	<b>MS (% Rec)</b>	<b>Duplicate (% RPD)</b>	<b>Blank Spike (% Rec)</b>
Alkalinity	75-125	< 20	80-120%
Chloride			for all
Nitrate			analytes
Sulfate			
Sulfide			
Total Organic Carbon (TOC) / Dissolved Organic Carbon (DOC)			

Attachment B

## **Field Sampling Plan Addendum**

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# 1.0 Introduction

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This Field Sampling Plan (FSP) Addendum describes in detail the sampling and data gathering methods and procedures for activities to be performed during the Supplemental Remedial Investigation/ Feasibility Study (RI/FS) (herein referred to as the SRI) for the Quanta Resources Superfund Site, Operable Unit 1 (OU1) (the Site). This FSP Addendum serves to update the original OU1 RI/FS FSP (Parsons, 2005) and subsequent addendums for those tasks not previously addressed. Except as otherwise noted herein, the work described in this document will be conducted in accordance with the applicable methods and procedures outlined in detail in the original FSP and relevant prior addendums. Collectively, these documents will be referred to herein as the FSP.

A detailed description of the Site setting, objectives, and identified data needs for the SRI are provided in the RI/FS Work Plan Addendum No. 4, to which this FSP Addendum is an attachment. The updated FSP should be used in conjunction with the revised Quality Assurance Project Plan (QAPP) (CH2M HILL, 2005; 2006a)<sup>1</sup> to guide all field and laboratory sampling and measurement conducted during the SRI. Together, the FSP and the revised QAPP comprise the Sampling and Analysis Plan (SAP) under the CERCLA RI/FS process.

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<sup>1</sup> The QAPP was amended most recently as part the RI/FS Work Plan Addendum No. 4 (CH2M HILL, 2008b) to which this document serves as an attachment to.

## 2.0 Sample Location and Frequency

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### 2.1 TarGOST® Profiling

TarGOST® response results for select locations will be used to identify impacted intervals for coal tar constituent soil sampling as discussed below in Section 3.7.1. Subsequent soil at select TarGOST® locations will be used to confirm the effectiveness of the TarGOST® technology and supplement existing data sets in order to complete the delineation of Site-related constituents and quantify potential risks associated with current and future uses at properties within the extent of OU1.

Details on the applicability and methods associated with the use of the TarGOST® screening tool have been provided previously in the RI/FS Work Plan Addendum No. 1 (CH2M HILL, 2006b). Unless otherwise noted below, all TarGOST® profiling work will be performed in accordance with the procedures provided in that document.

- Proposed TarGOST® profiling locations are illustrated in the attached Figure B-1. All proposed TarGOST® screening locations and their relevant DQOs are summarized by location in Table 1 of the RI/FS Work Plan Addendum No. 4.
- In order to maintain a consistent boring identification system and assure sufficient coverage using the TarGOST® screening tool, the existing grid system developed as part of the RI/FS Work Plan Addendum No. 1 has been extended across the entire Block 93 area and the northern portion of the former Lever Brothers property (Figure B-1).
- Throughout this grid, a total of 22 proposed TarGOST® borings have been positioned to confirm and delineate the presence of non-aqueous phase liquid (NAPL) detected in the southern portion of Block 93 North (SB-27 and SB-30), as well as NAPL previously detected and not delineated at Block 93 South and the northwestern portion of the former Lever Brothers property. In addition, two locations in the northeastern corner of the former Lever Brothers property have been proposed in order to confirm whether NAPL observed in soil in the vicinity of a former above ground storage tank (AST) once located along the shoreline here, is NAPL coal tar.
- Proposed TarGOST® locations and grid spacing for each property are based on the current understanding of the distribution of NAPL, the size of each property and anticipated accessibility of drilling locations.

### 2.2 Direct-Push Drilling and Soil and Groundwater Grab Sampling

Following the completion of the TarGOST® profiling work direct-push borings with continuous soil sampling will be advanced to depths of up to 30 feet below ground surface (bgs) at twenty-five (25) locations at the Quanta property, Block 92.01, Block 93 North, Central, South, Block 94, northern portions of the former Lever Brothers property and

within the intersection of Gorge Road and River Road. In order to collect undisturbed soil samples for SEP analyses 2 borings (a shallow and a deeper) will be drilled at one of these proposed locations. Borings will be advanced for the purpose of characterizing soil conditions and collecting soil and groundwater grab samples. Locations of proposed direct-push soil sampling and groundwater grab sampling are illustrated on Figure B-1.

## **2.3 Rotasonic Drilling, Soil Screening, Sampling**

Following the completion of the direct-push drilling, soil sampling and groundwater grab sampling soil borings will be advanced using rotasonic drilling techniques at a total of twenty-one (21) locations at the Quanta property, Block 93 Central, South, Block 94, the former Celotex property, the former Lever Brothers property, and within the intersections of Gorge Road and Old River Road and Gorge Road and River Road. In order to collect undisturbed soil samples for SEP analyses 2 borings (a shallow and a deeper) will be drilled at 9 of these proposed locations. Borings will be advanced for the purpose of characterizing soil conditions, collecting soil samples and/or installing monitoring wells or nested piezometers. Locations of the proposed rotasonic borings are illustrated on Figure B-1.

## **2.4 Monitoring Well and OU1 Piezometer Installations**

Twelve (12) 2-inch diameter and two (2) 4-inch diameter monitoring wells will be installed in fourteen (14) of proposed rotasonic borings across each of the properties throughout OU1. Nested piezometers each consisting of three (3) discrete monitoring points screened at varying depths will be installed at three (3) additional proposed rotasonic boring locations behind the wooden bulkhead at OU1. Locations of the proposed monitoring wells and nested piezometers are illustrated on Figure B-1.

## **2.5 Groundwater Monitoring**

After the completion of all soil and groundwater grab sampling and monitoring well installation activities proposed as part of the SRI, two (2) additional rounds of groundwater monitoring will be performed in 2008 across the Site on a semi-annual basis. Monitoring will include groundwater elevation and NAPL thickness measurements at all available wells and staff gauges as well as sampling of all newly installed wells and a subset of existing wells. Locations of all monitoring wells and gauges to be included in the groundwater monitoring events are included in Figure B-2.

- A total of forty-six (46) monitoring wells (33 existing and 13 newly installed wells) will be sampled during the first semi-annual groundwater sampling event.
- A total of thirty-eight (38) monitoring wells (25 existing and 13 newly installed wells) will be sampled during the second semi-annual groundwater sampling event.

## **2.6 Geophysical Surveys**

The geophysical survey to be conducted to evaluate the bulkhead and the adjoining area is designed to be conducted in two phases involving complementary surface geophysical survey and downhole techniques. The approach and ordering of the work is intended to produce data in an efficient manner such that subsequent work may be refined or eliminated based on early results. The approach involves decisions points relating to the implementation of both surface and down-hole ground penetrating radar (GPR) work based upon electromagnetic induction (EM) and electrical resistivity (ER) findings. The field plan is described in further detailed below. Locations and areas where geophysical surveying is proposed are illustrated on Figure B-3.

## **2.7 Trident Probe Survey**

The Trident Probe is a direct-push, integrated temperature sensor, specific conductance sensor, and pore water sampler developed to screen sites for areas where groundwater may be discharging to a surface water body. Differences in observed specific conductance and temperature indicate areas where groundwater discharge is occurring. Downgradient of dissolved phase coal tar and arsenic contamination in groundwater at OU1, up to fifty-five (55) Trident Probe locations will be used to measure temperature and specific conductance at a depth of two (2) ft below the sediment water interface and in surface water at one (1) ft above the surface water and sediment interface. Proposed Trident Probe locations are illustrated on Figure B-4 of the RI/FS Work Plan Addendum No. 5. Details on Trident Probe survey data collection procedures are provided below in Section 3.10.

## **2.8 Shallow Pore Water and Surface Water Sampling**

Following the analysis of temperature and specific conductance data at all Trident Probe survey locations pore water samples will be collected at up to five (5) Trident Probe survey locations where data evaluations indicate upwelling appears to be the most significant. At each location pore water samples will be collected from a depth of approximately 0.5 to 1 foot below the surface water and sediment interface using the Trident pore water sampling probe. At the same time surface water samples will also be collected at these five locations. Exact locations of the shallow pore water and surface water sampling will be determined in the field following the completion of the Trident Probe Survey. Details on Trident Probe pore water and surface water collection procedures are provided below in Sections 3.11, 3.12 and 3.13.

## **2.9 OU2 Piezometer Installation and Sampling and Hydraulic Head Measurements**

Following the completion of the Trident Probe survey, nested drive-point piezometers will be installed at five (5) locations within OU2 in order to collect groundwater samples and hydraulic head information downgradient of documented dissolved phase constituents at OU1 at varying depths below the sediment surface. The approximate locations of the

proposed piezometer nests at OU2 are illustrated on Figure B-4. Final locations may vary slightly in order to accommodate near shore areas that show a high likelihood of groundwater upwelling based on the Trident Probe survey work. Details on the OU2 piezometer installation, sampling, and hydraulic head measurements survey data collection procedures are provided below in Sections 3.14 through 3.15.

## 3.0 Sample Equipment and Procedures

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### 3.1 TarGOST® Profiling

Details on the applicability and methods associated with the use of the TarGOST® screening tool have been provided previously in the RI/FS Work Plan Addendum No. 1 (CH2M HILL, 2006b). Unless otherwise noted below, all TarGOST® profiling work will be performed in accordance with the procedures provided in that document.

- At each of the 22 locations, a TarGOST® outfitted probe will be driven into the ground using a Geoprobe® or similar direct-push drill rig to a depth that corresponds with the top of the silty-clay confining layer as previously determined during numerous historical conventional drilling events in each of these areas.
- Between locations the TarGOST® probe will be decontaminated using the sampling equipment decontamination procedure outlined in Section 3.2.4 of the original FSP (Parsons, 2005). Following each decontamination, the calibration of the TarGOST® tool will be checked using the reference emitter (RE).
- If refusal is encountered before completing the boring to within 2 feet of the desired depth, the location may be moved up to 10 feet in any direction from the original location. The depth of the top of the silty-clay confining unit in the areas where work is proposed is anticipated to range between 15 and 30 feet bgs.
- To ensure that the peripheral extents of coal tar are established as part of this work, a total of seven (7) contingency TarGOST® profile locations (Figure B-1) will also be pre-marked and cleared for utilities prior to mobilization. Once all the proposed locations for a given property have been profiled using TarGOST®, contingency locations adjacent to any areas requiring further delineation will be advanced until the extent of NAPL has been defined or drilling access limitations are encountered.
- Confirmatory soil sampling will be conducted at a total of twelve (12) TarGOST® locations (Figure B-1). These soil samples will also be used to delineate the extent of Site-related constituents across each of these properties, and where applicable will be used as part of the Human Health Risk Assessment (HHRA) for Block 93 Central and South. Details on the drilling and soil sampling methodologies are provided in the following sections.

### 3.2 Direct-Push Drilling

All direct-push drilling work will be performed in accordance with the procedures provided original RI/FS Field Sampling Plan (Parsons, 2005) and the RI/FS Work Plan Addendum No. 1 (CH2M HILL, 2006b) unless noted below.

- At each of the proposed direct-push drilling location continuous soil samples will be collected using a 4-foot long macro sampler with clean disposable acetate liners.
- All borings will be advanced to a depth of no greater than 3 feet into the top of the silty-clay or to the top of bedrock in areas where the silty-clay is not present.
- Soil samples will be screened using the jar-headspace screening technique with a photoionization detector (PID) equipped with a 10.2 electron volt bulb for the detection of ionizable compounds. Each device will be calibrated according to the manufacturer's operating manual in accordance with the original Field Sampling Plan (Parsons, 2005b), and the current Site-specific Health and Safety Plan.
- The presence of non-aqueous phase liquid (NAPL) within the soils at each location will be based on visual observations, PID screening results, and subsequent laboratory analytical data. Sudan IV or UV Fluorescence testing of soils with PID screening results greater than 100 part per million volume (ppmv) will not be performed due to the ineffectiveness of this method in prior RI/FS investigation activities at the Site.
- Visual observations indicating potential soil impacts including but not limited to NAPL, soft tar, hard tar, staining, sheens, fibrous paper, coal, slag, cinders, and reddish-purple discolorations will be made and recorded on the soil boring log. Visual observations of NAPL will be carefully recorded and correlated to the TarGOST® profile at that location if applicable.
- Soils will be described using the Unified Soil Classification System for the project record.
- All sampling devices and drilling equipment coming in contact with soil will be decontaminated between each boring in accordance with the methods specified in Section 3.2 of the original FSP (Parsons, 2005).
- Laboratory analyses and target soil sampling intervals for all direct-push drilling locations are specified in Tables 2 and 3 of the RI/FS Work Plan Addendum No. 4. Soil sample collection procedures are discussed below in the Soil Sampling Collection section.
- Following the completion of each direct-push boring the hole will be backfilled with bentonite or cement/bentonite grout in accordance with Section 5.7 of the original FSP (Parsons, 2005). In paved areas, the last 4 inches of each boring will be topped with asphalt cold-patch.
- Any drill cuttings and used acetate liners will be disposed of in accordance with Section 3.3 of the original FSP.

### **3.3 Groundwater Grab Sampling**

- Groundwater grab samples will be collected during advancement of the direct-push boring once a depth corresponding to the bottom of the proposed well screen has been reached.



- A 1-inch diameter polyvinyl chloride (PVC) temporary well point (TWP) will be installed within the borehole. Each well point will be constructed with a 5 foot long pre-packed machine-slotted PVC well screen spanning the interval from 0.5 feet above the water table to 4.5 feet below the water table.
- Immediately following installation of each TWP, the depth to water will be measured from ground surface, and groundwater will be purged and sampling using a peristaltic pump and dedicated polyethylene tubing using Low Flow sampling procedures previously employed at the Site, and as described in detail in Appendix A of the original RI/FS Field Sampling Plan (Parsons, 2005).
- Groundwater grab samples will be analyzed for volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs), and target analyte list (TAL) metals (see Table 5 of the RI/FS Work Plan Addendum No. 4).
- Following the completion of groundwater grab sampling, temporary well materials will be removed and the hole and the boring will be backfilled with bentonite or cement/bentonite grout in accordance with Section 5.7 of the original FSP (Parsons, 2005). In paved areas, the last 4 inches of each boring will be topped with asphalt cold-patch.

### 3.4 Rotasonic Drilling

- Each proposed rotasonic boring will be completed by continuously advancing a 4-inch core barrel and 6-inch override casing through the subsurface soils to the desired installation depth.
- At locations where monitoring wells are to be installed the 6-inch override casing will be temporarily left at the base of the boring to serve as an isolation casing during well construction.
- At each location continuous soil samples will be retrieved in five foot intervals using the 4-inch diameter stainless steel rotasonic core barrel with clean disposal Lexan® liners.
- Soil samples will be screened using the jar-headspace screening technique with a photoionization detector (PID) equipped with a 10.2 electron volt bulb for the detection of ionizable compounds. Each device will be calibrated according to the manufacturer's operating manual in accordance with the original Field Sampling Plan (Parsons, 2005b), and the current Site-specific Health and Safety Plan.
- The presence of non-aqueous phase liquid (NAPL) within the soils at each location will be based on visual observations, PID screening results, and, in some cases, subsequent laboratory analytical data. Sudan IV or UV Fluorescence testing of soils with PID screening results greater than 100 ppmv will not be performed due to the ineffectiveness of this method in prior RI/FS investigation activities at the Site.
- Visual observations indicating potential soil impacts including but not limited to NAPL, soft tar, hard tar, staining, sheens, fibrous paper, coal, slag, cinders, and reddish-purple discolorations will be made and recorded on the soil boring log. Visual observations of

NAPL will be carefully recorded and correlated to the TarGOST® profile at that location if applicable.

- Soils will be described using the Unified Soil Classification System for the project record.
- All sampling devices and drilling equipment coming in contact with soil will be decontaminated between each boring in accordance with the methods specified in Section 3.2 of the original FSP (Parsons, 2005).
- Laboratory analyses and target soil sampling intervals for all rotasonic drilling locations are specified in Tables 2 and 3 of the RI/FS Work Plan Addendum No. 4. Soil sample collection procedures are discussed below in the Soil Sampling Collection section.
- Following the completion of each rotasonic boring that will not be completed as a monitoring well, the boring will be backfilled with a cement/bentonite grout in accordance with Section 5.7 of the original FSP (Parsons, 2005). In paved areas, the last 4 inches of each boring will be topped with asphalt cold-patch.
- Any drill cuttings and used Lexan® liners will be disposed of in accordance with Section 3.3 of the original FSP.

### 3.4.1 Shallow Borings

At fourteen (14) locations rotasonic borings will be advanced to a depth of no greater than 3 feet into the top of the silty-clay or to the top of bedrock in areas where the silty-clay is not present (anticipated to be no greater than 30 ft. bgs) using rotasonic drilling techniques. At nine of these locations a second, shallower boring (between approximately 10 and 15 ft. bgs) will also be advanced within 3 feet of the original boring in order to allow for the collection of SEP samples for arsenic (see Section 3.7.2).

### 3.4.2 Deeper Borings (shoreline area)

At the remaining seven (7) rotasonic locations, BH-1 through 3, PZ-6 through 8, and MW-135 along the shoreline, borings will be advanced through the silty-clay (if present) to the top of bedrock (anticipated to be between 35 and 50 feet bgs) in order to confirm the vertical delineation of NAPL near the shoreline.

At each of these locations penetration of a silty-clay and/or peat layer with an anticipated thickness of 5 to 20 feet is anticipated beginning at approximately 13 feet. In order to prevent migration of groundwater and other potentially mobile substances into the silty-clay aquitard and below during and after drilling and well construction a multi-case override system unit will be required to isolate and seal off the shallow water bearing. Sonic drilling methods substantially reduce the friction of the soil immediately surrounding the advancing core barrel or casing. Once the Sonic energy is stopped, however, the soil reforms adjacent to the pipe. If this is done within a confining layer, the re-formed soil actually creates a seal against the casing wall.

The multi-case override isolation method will be performed as follows:

- Step 1: A six-inch borehole will be cored and cased approximately 1 foot into the silty-clay confining layer.

- Step 2: A seven-inch casing will be sonically drilled 2 feet into the confining layer over the six-inch casing completed as part of step 1. Both casings will then be sealed and pressurized with water or air for a period of time to check for leakage in order to confirm that a seal exists between the seven-inch temporary casing and surrounding formation.
- Step 3: Sonic coring and casing a six-inch borehole to depth inside of the seven inch casing will then be resumed. No Sonic energy will be applied to the seven-inch casing.
- Step 4: Where applicable, well materials will be installed (screen, riser pipe, gravel pack, seal, and grout).
- Step 5: The boring/well will be completed by removing the six-and seven-inch Sonic casings in reverse order (first the six, then the seven-inch) while sonic energy is being applied to the casings (Figure 2).

Additional information on the proposed borehole isolation method described above is included in Attachment B-1 of the FSP.

### 3.5 Monitoring Well Installation

- Two 4-inch diameter and 12, 2-inch diameter monitoring wells will be constructed using 10-foot long 0.020-inch machine slotted, flush-threaded schedule 40 PVC screens, sumps, and risers. Information on the proposed diameter and screened interval for each monitoring well is provided in Table 4 of the RI/FS Work Plan Addendum No. 4.
- All monitoring wells will be screened within the unconfined water bearing unit. Exact screen intervals will depend on the objectives of each well as specified in Table 4 of the RI/FS Work Plan Addendum No. 4. Anticipated screen intervals for each well are provided in Table 4. However, for MW-123 and MW-135 (4-inch wells) where an objective is to assess the mobility of NAPL known to be present in these areas, the final screen depth may be adjusted to span the interval of NAPL observed during rotasonic drilling.
- At each monitoring well the screen shall be sand packed using 20/40-sieve size sand pack or approved alternate to a depth that corresponds to 2 feet above the top of the well screen, a 2-foot bentonite seal shall be placed on top of the sand pack in the annulus of the hole, the remainder of the annulus will be cemented to the surface using a portland cement that contains up to 8% bentonite by weight. Each well will also be constructed with a 2-foot long sump installed at the base of the borehole beneath the screen and backfilled with bentonite to a depth of 6-inches below the base of the bottom of the screen.
- After allowing the grout placed within the annulus of each borehole to cure for a minimum of 24 hours each monitoring well will be developed in accordance with the original RI/FS Field Sampling Plan (Parsons, 2005).

### 3.6 OU1 Shoreline Piezometer Installation

- At each of the three (3) nested piezometer locations at OU1 (PZ-6 through 8) individual piezometers will be constructed within a single borehole using 1-inch and 2-inch diameter 2-foot long 0.020-inch machine slotted, flush-threaded schedule 40 PVC screens, sumps, and risers. Information on the proposed diameter and screened interval for each piezometer is provided in Table 7 of the RI/FS Work Plan Addendum No. 4. The deepest piezometer in each cluster will be constructed with 2-inch diameter screens and risers and the remaining 2 points within each hole will be constructed with 1-inch diameter materials.
- Exact screen intervals will depend on the objectives of each well and the results of the phase 1 geophysical surveys in the area of the wooden bulkhead. Anticipated screen intervals for each piezometer are provided in Table 7.
- Each piezometer screen shall be sand packed using 20/40-sieve size sand pack or approved alternate to a depth that corresponds to 2 feet above the top of the well screen, a 2-foot bentonite seal shall be placed on top of the sand pack in the annulus of the hole, the remainder of the annulus will be cemented to the surface, or 2 feet below the bottom of the next piezometer screen interval using a portland cement that contains up to 8% bentonite by weight. Attempts will be made to avoid screening any piezometer within the silty-clay unit. The preference, if this unit is present, will be to screen wells discretely, above (at 2 intervals), and below the aquitard (at one interval).
- After allowing the grout placed within the annulus of each borehole to cure for a minimum of 24 hours each monitoring well will be developed in accordance with the original RI/FS Field Sampling Plan (Parsons, 2005).

### 3.7 Soil Sample Collection

#### 3.7.1 VOC, SVOC, PCBs and TAL Metals

For direct-push and rotasonic borings where VOC, SVOC, PCB, and TAL metals analyses are proposed, target sampling intervals for each location are specified in Table 2 of the RI/FS Work Plan Addendum No. 4.

- At twenty-one (21) borings (16 direct-push and 5 rotasonic) a total of two (2) samples will be collected for VOC, SVOC, PCB and TAL Metals analysis from each boring (see Table 2 of the RI/FS Work Plan Addendum No. 4). One sample will be collected from the unsaturated soil interval between 0 and 2 feet bgs that appears most affected, based on soil screening results and/or visual observations. The second sample will be collected from between 2 and 10 feet bgs at the specific depth interval where TarGOST® results and/or PID screening results and visual observations indicate the greatest impacts are present. A third sample may be collected from depths greater than 10 feet bgs if TarGOST® results or visual impacts indicate NAPL is present and isolated from soils at 10 feet bgs or less.
- At each of the six (6) borings across the intersections Gorge Road and River Road and Gorge and Old River Road, and Block 92.01 (4 direct-push and 2 rotasonic), two samples

will be collected for VOC, SVOC, PCB and TAL Metals analysis. One sample will be collected from the unsaturated soil interval (anticipated to be between 0 and 4 feet bgs) and a second sample will be collected from the saturated interval. Discrete sampling depths for both samples will target the most impacted soils based on soil screening results and/or visual observations.

- At each of the remaining four (4) direct-push soil sampling locations at the former Lever Brothers property one sample will be collected for VOC, SVOC, PCB and TAL Metals analysis from each boring from the discrete interval where TarGOST® results and/or PID screening results and visual observations indicate the greatest impacts are present. At two of these borings (northeast corner of the former Lever Brothers property) soil samples will also be collected and analyzed for total petroleum hydrocarbon (TPH) fingerprinting using the method specified in the revised QAPP.

### 3.7.2 Arsenic Sequential Extraction Procedure

For direct-push (1) and rotasonic (9) borings where arsenic sequential extraction procedure (SEP) analysis is proposed, target sampling intervals for each location are specified in Table 3 of the RI/FS Work Plan Addendum No. 4.

- At one (1) direct-push boring and nine (9) rotasonic boring locations samples will be collected for arsenic SEP. Target sampling intervals for SEP samples are summarized in Table 3 of the RI/FS Work Plan Addendum No. 4 and may differ from those collected for organic and metals analysis.
- Two (2) samples (a 'shallow' and a 'deeper' sample) will be collected for SEP analyses at each of the eleven (11) proposed SEP locations. All samples will consist of a 1 ft. long, in-tact, sealed core collected from saturated soils from within the depth intervals specified in Table 3 of the RI/FS Work Plan Addendum No. 4.
- To determine the exact 'shallow' sample interval a pilot hole will be drilled to the maximum possible depth of the specified shallow sample interval for each boring (maximum of 15 feet bgs). Where applicable this boring will be used to collect samples for VOCs, SVOCs, PCBs, and TAL Metals as specified above in Section 3.7.1. In the case of SEP samples being collected at the proposed MW-130A and B well cluster the shallower "A" well will serve as the 'shallow' boring at this location.
- Characterization of soils within each of these pilot holes will be used to determine the exact interval for collection of the 'shallow' arsenic SEP sample. The one foot interval within the specified target sample interval for the boring that shows the highest likelihood for metals impacts (e.g. reddish-purple soil, cinder, slag, or coal) will be targeted for sampling during the advancement of the second boring at that location. The core run in which this interval is retrieved will begin at a minimum of 1 ft. above the target interval and end at a minimum of 1 ft. below the target interval.
- Once the 'shallow' sample is retrieved from the second boring at a given location using a clean disposable acetate or Lexan® core sleeve, the 1 ft. interval comprising the 'shallow' sample interval will be severed from the rest of the core and capped immediately to minimize disturbance and oxygenation during shipment and handling.

- For the 'deeper' sample the second boring at each location will continue to be advanced until the 'deeper' sample interval as specified in Table 3 of the RI/FS Work Plan Addendum is encountered. The core run in which this interval is retrieved will begin at a minimum of 1 ft. above the target interval and end at a minimum of 1 ft. below the target interval.
- Once the sample is retrieved from the boring using a clean disposable acetate or Lexan® core sleeve, the 1 ft. interval comprising the 'deeper' sample interval will be severed from the rest of the core and capped immediately to minimize disturbance and oxygenation during shipment and handling.

## **3.8 Semi-Annual Groundwater Monitoring**

### **3.8.1 Sample Collection**

The parameters for which each groundwater sample will be analyzed during each of the two semi-annual monitoring events are specified by well in Table 5 of the RI/FS Work Plan Addendum No. 4.

- Groundwater samples will be collected during the first semi-annual groundwater sampling event will be analyzed for dissolved TAL metals, additional major ions, alkalinity, and DOC from a total of forty-six (46) wells.
- A subset of 36 wells will also be sampled for VOCs, SVOCs during the first semi-annual event. Samples collected from newly installed wells will also be analyzed for PCBs during the first event only.
- A further subset of 19 wells will also be sampled for arsenic III and V speciation during the first semi-annual event.
- Groundwater samples collected during the second semi-annual groundwater sampling event will be analyzed for VOCs, SVOCs (36 wells). These 36 wells plus two additional wells (38 total) will also be sampled for dissolved arsenic, iron, and lead.

With the exception of the samples that will be collected for arsenic III and V speciation during the first semi-annual event, all groundwater samples will be collected using the equipment and procedures previously employed at the Site as part of RI/FS groundwater sampling activities, and as described in detail in Appendix A of the original RI/FS FSP (Parsons, 2005).

Monitoring well purging procedures for arsenic III and V speciation will be the same as those for all other parameters. However, specialized equipment and procedures are required for filling the sample bottles to insure oxidation state of the sample is preserved. These procedures are as follows:

- The bottom of a large sample cooler, preferably 23" x 14" x 14" (WxLxH) or larger, is covered with dry ice and approximately 500mL of water. The lid to the cooler should remain closed until samples are ready to be collected.

- One person ("dirty hands") pulls a bagged bottle from the cooler and opens the outer, dirty bag, avoiding touching inside that bag.
- The other person ("clean hands") reaches in, opens the inner bag (if present), and pulls out the sample bottle. "Clean hands" should not touch anything but the sample bottle, its cap, and the water being sampled.
- The bottle is opened and (uncapped) then submerged into air space of the anoxic handling vessel and inverted SLOWLY five times. At this point, the sample bottle must never leave the confines of the anoxic handling vessel until the entire sampling procedure is complete.
- One vial of preservative should be added to the sample bottle at this time. The vial contains a buffered solution of ethylene diamine tetraacetic acid (EDTA) which chelates with the iron. Depending on conditions, arsenate has a high sorption efficiency with iron precipitates and may coprecipitate resulting in biased results; therefore, chelation with a buffered EDTA solution is recommended to minimize arsenic loss during sampling and transport.
- The pump tubing should be primed by another sampling technician prior to sample collection to account for residual oxygen in the tubing which may oxidize As(III) to As(V). Approximately 500mL of sample should be pumped out of the tubing prior to sample collection.
- The sample container is filled until zero headspace is present (the tubing end must be brought into the anoxic handling vessel). If the sample is designated as a field spike, approximately 10mL of headspace should be left in the sample bottle to account for the spike volume. Any field spike should be added at this time to monitor for speciation conversion during sample shipment and analysis.
- The sample bottle is then immediately resealed. The sample bottle should be squeezed to ensure a tight seal. Invert the sample bottle three times to ensure proper mixing of the preservative and the field spike (if added). The bottle is then re-bagged in the opposite order from which it was removed.
- The lid to the anoxic handling vessel is then replaced to minimize carbon dioxide loss.
- Nitrile gloves are changed between samples and whenever anything not known to be trace metal clean is touched.
- Field parameters measured as part of the low flow stabilization documentation should be reanalyzed and recorded at each location after the sampling is completed to document any changes that may have occurred during the sampling process.

### 3.8.2 Groundwater and Product Thickness Measurements

Prior to the commencement of each of the two semi-annual groundwater sampling events, synoptic water level and product thickness measurements will be conducted at all newly sampled and accessible existing monitoring wells previously monitored during the RI/FS. If wells are not accessible at the time of measurement a note will be made in the field as to why the well could not be measured at that time.

Groundwater gauging will be performed during mid-tide conditions over a period of time no greater than 4 hours. Measurements will be performed by three field personnel simultaneously commencing measurements at those wells closest to the Hudson River and progressing towards the east across the Site.

## **3.9 Geophysical Surveys**

### **3.9.1 Phase 1 (Surface Geophysical Survey and Down-hole Test)**

Surface geophysical techniques to be employed include multi-frequency electromagnetic induction (EM), electrical resistivity (ER), and ground penetrating radar (GPR) profiling as follows:

- Conduct visual inspection of the area, locating any evidence of the wooden bulkhead and possible extensions. Record this information scaled field site plan. Identify and map locations of visual evidence of surface and subsurface features or cultural materials (e.g. concrete, asphalt, metal containing debris) that may affect geophysical survey measurements.
- Establish survey grid area, anticipated to be approximately 300 feet by 300 feet and including the wooden bulkhead and an area inboard of the bulkhead, utilizing a global positioning system (GPS). The proposed area of the survey is identified in Figure B-3.
- Conduct frequency-domain EM survey work and field process data. These EM data will be collected utilizing a Geophysical Survey Systems Incorporated EMP Profiler (EMP-400) multi-frequency terrain conductivity meter.
- The EM survey will involve vertical dipole instrument orientation and include quadrature phase (proportional to terrain conductivity) and in-phase (metal sensitive) data collection using coil alignments parallel to and perpendicular to the shoreline at three frequencies 4,410 Hz, 9,810 Hz and 15,030 Hz, collected simultaneously. Data density will be equivalent to a minimum of 5 ft centers over the survey area. The instrument has integrated GPS capabilities and will enable rapid data collection and subsequent where access by an operator on foot is readily available.
- EM field data will be interpolated and contoured during the field mobilization with Surfer (Golden Software) or equivalent contouring package. Mapped EM data will be used to initially interpret the presence of the wooden bulkhead and possible inboard bulkheads, supporting field decisions concerning final locations for ER and GPR transects.
- Three (3) ER transects up to 250' in length and parallel to the shoreline in the vicinity of the bulkhead and three (3) to five (5) ER transects up to 200' in length and perpendicular to the shoreline will be located based upon field observations and EM profiling results. Final electrode array type and location will be established based upon EM results and field conditions.
- Conduct ER profiling and inversion modeling. This will involve an Advanced Geosciences, Inc. SuperSting R1 Earth Resistivity/IP System or similar with roll-along



capability for 56 stainless steel electrodes and take-out cables. It is likely dipole-dipole arrays will be established.

- Provided that subsurface materials are electrically resistive enough, in other words bulk terrain conductivities identified during the EM survey are generally low (<100 mmhos/meter), then GPR survey work will be conducted.
- If GPR work is conducted then transects, generally perpendicular to the wooden bulkhead will be established. This is so forward-focused signal reflections off the base and length of the bulkhead may be evaluated from GPR data collected as the antenna approaches the bulkhead from the landward side. Some transects perpendicular to the bulkhead may be needed to be established to evaluate GPR response to lateral changes in material properties in the vicinity of the bulkhead that may have been identified during the EM and/or ER surveys.
- Conduct GPR profiling. This work will involve a Geophysical Survey Systems Incorporated SIR 20 or SIR 3000 control unit. Antennae to be utilized will include a multi-frequency 16-80 MHz (Model 3200 MLF) operated in stacked sounding and continuous modes and a 400 MHz (Model 5103). Optional antennae include a 100 MHz High Power operated in monostatic and/or bistatic configurations (Model 3207/3207A) and a 270 MHz (Model 5104). Field determinations will be made whether or not to mobilize the optional antenna frequencies based upon results from initial work involving the multi-frequency 16-80 MHz (Model 3200 MLF) and 400 MHz antenna. The ultimate antenna frequencies/time-window settings utilized to complete this work will be those that best enable identification of the bottom of the bulkhead and evaluation of the lateral continuity of this structure. RADAN image processing software will be utilized to conduct GPR signal processing and enhancements.

A single down-hole test will also be conducted during Phase 1 at existing monitoring well MW-116DS as follows:

- A test of downhole GPR may be optionally conducted to evaluate the potential for detailed vertical profiling of the wooden bulkhead with this technique. A decision concerning whether or not to conduct the work will be based upon surface GPR and EM findings.
- If downhole GPR is conducted, existing monitoring well MW-116DS will likely be utilized. The borehole GPR survey is intended to measure signal reflections from horizontally transmitted and reflected radar signals that may be attributed to those off the bulkhead. This will provide information as to the viability of using this method at newly proposed boring (piezometer) locations along the bulkhead to be installed to support Phase 2.

### **3.9.2 Phase 2 (Additional Down-hole Tests)**

Surface geophysical surveys and the test of borehole GPR conducted during Phase 1 will be utilized to refine the locations of borings to be drilled as part of the monitoring well and OU1 piezometer installation activities described in Sections 3.5 and 3.6. Figure B-3 identifies potential locations for three (3) deep piezometers and one monitoring well planned, as part of the proposed work, for further down-hole geophysical evaluations. These four (4) new

installations will enable vertical seismic profiling (VSP) of the bulkhead. If the downhole GPR profiling is conducted in Phase 1 and proves successful, it may be utilized along with VSP, otherwise only VSP work will be conducted at the three locations. The downhole VSP work will be conducted as follows:

- Hydrophones will be deployed in each of the newly installed piezometers at multiple depths.
- A sparker seismic source will be located within the mud deposits on the river side of the bulkhead. Multiple shots will be initiated to enable data stacking and collection for a variety of geophone configurations. The seismic source may be located at more than one location to enhance the data set.

The VSP survey will evaluate disruption of raypaths from source to receiver associated with the presence of the bulkhead. The hydrophones in the piezometers will measure direct arrivals of ray paths for multiple depths and possibly multiple aspect angles relating to multiple source locations.

### 3.10 Trident Probe Survey

This section presents information on the Trident Probe system and the additional equipment and procedures to be used in order to determine areas of groundwater discharge to OU2. Subsequent pore water sampling using the Trident probe is discussed in detail in Sections 3.11 and 3.12. The use of a Trident probe was selected for the site because of the variability in water depths, and because samples need to be collected from precise intervals.

The Trident probe is a direct-push system equipped with three (3) distinct probes (temperature, specific conductance, and a pore water sampling probe) designed to penetrate the sediment surface at a prescribed depth. In addition, probes positioned above the sediment surface simultaneously measure temperature and specific conductance of surface water. The Trident Probe system is equipped with a metal plate that serves as a depth guide for probe insertion and prevents infiltration of surface water during pore water sampling. Contrasts in temperature and conductance between surface water and groundwater are used to determine likely areas of upwelling groundwater. The pore water sampling probe is used in conjunction with a peristaltic pump to collect samples for laboratory analysis in order to determine contaminant concentrations. The Standard Operating Procedure (SOP) for the Trident Probe system is provided as Exhibit B-1 and includes a diagram of the probe.

The survey will be performed from a boat during ebbing tidal conditions, beginning just after high tide and continuing until the surface water is no longer navigable by boat. At each of the fifty-five (55) Trident probe survey locations, the following procedure will be performed:

1. Anchor the boat to minimize movement during measurements/sampling.
2. Lower the Trident Probe through the water column and advance it to a depth of approximately 2 feet below the sediment surface.
3. Record the coordinates of the Trident Probe location using a GPS with sub-meter accuracy.

4. Record water depth (depth to top of sediment) using an acoustic sounder.
5. Record the hydraulic head of the pore water.
6. Record the depth to the surface water from the same measuring point used to measure the hydraulic head of the pore water.
7. Record the temperature and conductivity readings until stabilization in both the 21 ft. pore water and the surface water (measured at approximately 1 ft. above the sediment water interface) has been achieved. If pore water parameters are not distinguishable from surface water parameters, the Trident Probe will be repositioned and sampling repeated.
8. Once again, record water depth (depth to top of sediment) using an acoustic sounder.
9. Once again, record the hydraulic head of the pore water.
10. Once again, record the depth to the surface water from the same measuring point used to measure the hydraulic head of the pore water.
11. Retract the Trident probe and decontaminate as appropriate (see Trident Probe SOP in Exhibit B-1).

### 3.11 Pore Water Sampling

After completion of all Trident Probe survey locations the temperature and conductivity data from each will be reviewed to determine those five (5) locations showing the greatest likelihood of groundwater upwelling. Areas with significant groundwater seepage will be considered those locations showing the greatest variations in temperature and specific conductance between surface water and pore water. Depending on these data, consideration will also be given to areas where lateral variations in temperature and specific conductance of surface water and/or pore water indicate likelihood of groundwater upwelling. If necessary, preference should be given to those locations that are nearer shore and downgradient of the greatest observed contamination at OU1.

Pore water samples will be collected using the Trident Probe system as described above. Trident probes will be set to collect temperature and specific conductance readings and pore water samples at a depth of approximately 0.5 to 1 foot below the sediment/surface water interface. On-board measurement of oxidation-reduction potential (ORP), pH, and dissolved oxygen (DO) differentials in addition to the temperature and specific conductance differentials at depth will confirm whether short-circuiting of surface water across the sediment is occurring during purging. The Trident Probe's metal plate which is designed to sit above the pore water probe at the sediment surface will prevent infiltration of surface water during pore water sampling.

Pore water sampling will be performed from a boat during ebbing tidal conditions, beginning just after high tide and continuing until the surface water is no longer navigable by boat. At each of the five (5) pore water sampling locations, the following procedure will be performed:

1. Reposition the boat to the original Trident Probe location using the GPS and anchor the boat to minimize movement during measurements/sampling.
2. Lower the Trident Probe through the water column and advance it to a depth of approximately 1 foot below the sediment surface (such that the sample is collected between 0.5 and 1 foot below the sediment surface).
3. Record the coordinates of the Trident Probe location using a GPS with sub-meter accuracy.
4. Record water depth (depth to top of sediment) using an acoustic sounder.
5. Record the hydraulic head of the pore water.
6. Record the depth to the surface water from the same measuring point used to measure the hydraulic head of the pore water.
7. Continuously record the temperature and conductivity readings until stabilization in both the subsurface and surface water probes.
8. Begin purging of pore water into a closed flow-thru cell using a peristaltic pump and dedicated polyethylene tubing.
9. Measure and record specific conductance, temperature, as well as ORP, pH and DO in an oxygen-free flow thru cell at the surface. Simultaneously measure specific conductance, and temperature of the surface water and using the Trident Probe sensors. If variations in common parameters measured between surface water and pore water indicate that infiltration of surface water is occurring the probe will be repositioned and sampling will begin again.
10. Upon the collection of parameters as measured above and readings of specific conductance and temperature from the pore water and surface water Trident Probe sensors, collect samples for VOCs, SVOCs and dissolved arsenic in accordance with the methods specified in the revised QAPP (CH2M HILL, 2005; 2006b; 2008a).
11. Collect additional samples at each location for arsenic III and V speciation using the detailed sample collection method outlined below in Section 3.12. Samples for these analyses must be collected in an oxygen-free environment in order to preserve the original oxidation state of the pore water sample prior to analysis of arsenic III and V speciation using the NJDEP-approved ion chromatography method as specified in the revised QAPP (CH2M HILL, 2005; 2006b; 2008a).
12. Following the completion of sample collection, once again, record water depth (depth to top of sediment) using an acoustic sounder.
13. Once again, record the hydraulic head of the pore water.
14. Once again, record the depth to the surface water from the same measuring point used to measure the hydraulic head of the pore water.
15. Retract the Trident probe and decontaminate as appropriate (see Trident Probe SOP in Exhibit B-1).

### 3.12 Pore Water Sample Collection for Arsenic Speciation

Pore water purging procedures for arsenic III and V speciation will be the same as those for all other parameters. However, specialized equipment and procedures are required for filling the sample bottles to insure oxidation state of the sample is preserved. These procedures are as follows:

- The bottom of a large sample cooler, preferably 23" x 14" x 14" (WxLxH) or larger, is covered with dry ice and approximately 500mL of water. The lid to the cooler should remain closed until samples are ready to be collected.
- One person ("dirty hands") pulls a bagged bottle from the cooler and opens the outer, dirty bag, avoiding touching inside that bag.
- The other person ("clean hands") reaches in, opens the inner bag (if present), and pulls out the sample bottle. "Clean hands" should not touch anything but the sample bottle, its cap, and the water being sampled.
- The bottle is opened and (uncapped) then submerged into air space of the anoxic handling vessel and inverted SLOWLY five times. At this point, the sample bottle must never leave the confines of the anoxic handling vessel until the entire sampling procedure is complete.
- One vial of preservative should be added to the sample bottle at this time. The vial contains a buffered solution of EDTA which chelates with the iron. Depending on conditions, arsenate has a high sorption efficiency with iron precipitates and may coprecipitate resulting in biased results; therefore, chelation with a buffered EDTA solution is recommended to minimize arsenic loss during sampling and transport.
- The pump tubing should be primed by another sampling technician prior to sample collection to account for residual oxygen in the tubing which may oxidize As(III) to As(V). Approximately 500mL of sample should be pumped out of the tubing prior to sample collection.
- The sample container is filled until zero headspace is present (the tubing end must be brought into the anoxic handling vessel). If the sample is designated as a field spike, approximately 10mL of headspace should be left in the sample bottle to account for the spike volume. Any field spike should be added at this time to monitor for speciation conversion during sample shipment and analysis.
- The sample bottle is then immediately resealed. The sample bottle should be squeezed to ensure a tight seal. Invert the sample bottle three times to ensure proper mixing of the preservative and the field spike (if added). The bottle is then re-bagged in the opposite order from which it was removed.
- The lid to the anoxic handling vessel is then replaced to minimize carbon dioxide loss.
- Nitrile gloves are changed between samples and whenever anything not known to be trace metal clean is touched.

### 3.13 Surface Water Sample Collection

At each of the five (5) Trident Probe locations selected for shallow pore water sampling surface water samples will also be collected at the same time as the pore water samples.

- One surface water grab sample will be collected at each location. Samples will be collected 1 ft above the sediment surface.
- A peristaltic pump will collect the water samples using clean Tygon® tubing cut to an appropriate length and weighted with a downrigger to ensure vertical descent in the water column. The water will be pumped into laboratory-supplied, pre-cleaned containers for chemical analysis. Chemical analysis will include VOCs, SVOCs and dissolved arsenic.
- For the collection of the dissolved arsenic sample, filtering will be performed in the field while pumping using a 45 micron filter that will be replaced for each sample.

### 3.14 OU2 Piezometer Installation and Sampling

At each of the proposed piezometer locations at OU2 three (3) piezometers will be installed to depths of approximately 25, 15 and 5 ft. below the sediment surface. At each piezometer location, the following procedure will be performed:

1. Each piezometer will be installed during low-tide conditions using a slide-hammer or electric hammer when the near-shore mudflat is exposed and locations can be accessed using temporary plywood walkways. Nearshore piezometers (PZ-2) adjacent to the bulkhead will be installed and accessible from the existing concrete overhang at OU1.
2. Piezometer tips will consist of 3/4 inch stainless steel 0.5 ft. long wire screened probe coupled to 1/2 inch ID Teflon® sample tubing and driven using 3/4 inch steel pipe extensions.
3. The deeper piezometer will be installed to the maximum depth possible (anticipated to be 25 ft. below sediment surface). Subsequent, collocated shallower piezometers at each location will be installed at increasingly shallower depths in order to achieve uniform depth coverage at that location. No piezometer shall be installed to a depth shallower than 5 ft. below sediment surface.
4. Each piezometer will be completed with an extension above the sediment surface that is sufficient to prevent submersion by surface water during high-tide conditions.
5. Following installation the depth to water will be measured inside the Teflon tubing within each piezometer using a small diameter (1/4 inch) electronic water level probe.
6. The elevation of each probe will be measured relative to the North American Vertical Datum of 1988 (NAVD 88) using a survey rod and level and a known benchmark at OU1 (near shore monitoring well measuring point elevation). The lateral location of each piezometer cluster will be recorded using a GPS with sub-meter accuracy using the North American Datum of 1983 (NAD 83) New Jersey State Plane coordinate system.

7. Pore water samples will be collected from each of the piezometers during low-tide conditions when near-shore mudflat is exposed and locations can be accessed using temporary plywood walkways.
8. Begin purging of pore water into a closed flow-thru cell using a peristaltic pump and dedicated polyethylene tubing.
9. Measure and record specific conductance, temperature, as well as ORP, pH and DO in an oxygen-free flow thru cell at the surface.
10. Following the collection of parameters pore water samples will be collected for VOCs, SVOCs, and dissolved arsenic in accordance with the methods specified in the revised QAPP (CH2M HILL, 2005; 2006b; 2008a).

### 3.15 Shoreline Hydraulic Head Measurements

Following the installation of the nested piezometers water levels will be collected from all newly installed piezometers at both OU1 and OU2 up to 6 times over both high and low tide conditions over a period of one week. When not accessible from the shoreline or by temporary plywood walkway, hydraulic head measurements at piezometers will be collected by boat. All measurements will be collected in conjunction with water elevation data at the existing staff gauge within the Hudson River and at all available monitoring wells at OU1 adjacent to the shoreline.

### 3.16 Utility Markout

- Prior to beginning any drilling activities associated with the SRI, all proposed investigation locations as described below and illustrated in Figure B-1 will be field located and marked in the field by a Licensed New Jersey Surveyor.
- A geophysical survey using ground-penetrating radar and/or electromagnetic conductance will be performed in the area of all proposed locations prior to drilling. Identified subsurface structures will be marked in the field and on a map by the geophysical survey contractor. In addition, as part of the necessary access agreements required for performing this work, plans of available subsurface utilities on each of the offsite properties will be obtained and reviewed in context of the geophysical survey results.
- Based on this information, proposed TarGOST® and other boring locations will be moved to avoid subsurface structures. This survey work will be performed in advance of mobilization of any drilling equipment to allow for the proper relocation of proposed boring locations where necessary.
- In addition to the private utility survey/markout, New Jersey One Call will be contacted at least 3 working days and not more than 10 working days before initial mobilization of drilling equipment to the Site so that they may also clear utilities for the area.

### 3.17 As-Built Survey

- Following their completion the lateral location and ground surface elevation of all TarGOST® profile locations, direct-push borings, rotasonic borings will be surveyed by a Licensed New Jersey Surveyor using the North American Vertical Datum of 1988 (NAVD 88) and the North American Datum of 1983 (NAD 83) New Jersey State Plane coordinate system.
- The ground elevation, protective casing elevation, and top of the PVC riser pipe elevation and lateral location of each monitoring well will also be surveyed relative to the coordinate systems referenced above.
- At the same time that newly completed soil borings and monitoring wells are surveyed a Licensed New Jersey Surveyor will locate property boundaries, building locations, curbing, walkways, and at grade utility features and perform a topographic survey of the Block 93 Central, Block 93 South, and the eastern portions of Block 94 to compliment the existing survey plan.



## 4.0 Sample Handling and Analysis

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- Quality assurance /quality control (QA/QC) samples will be collected at the frequency specified in the revised QAPP (CH2M HILL, 2005; 2006a).
- Soil and groundwater samples analyzed for VOCs, SVOCs, PCBs, TAL Metals geochemical parameters, arsenic SEP analysis and arsenic speciation via ion chromatography will be analyzed in accordance with the methods specified in the revised QAPP as amended most recently with the text and tables provided as part of Attachment A of the RI/FS Work Plan Addendum No. 4.
- Sample labeling, handling, packaging, and shipment will be performed in accordance with the procedures identified in the original RI/FS Field Sampling Plan (Parsons, 2005b), unless otherwise specified below.
- With the exception of arsenic SEP analysis for soil and arsenic III and V speciation, all soil and groundwater samples will be shipped to Accutest Laboratories of Dayton, New Jersey via overnight courier under executed chain-of-custody.
- Soil samples for arsenic SEP analysis and groundwater samples for arsenic III and V speciation in groundwater will be shipped overnight to Applied Speciation and Consulting, LLC of Tukwilla, Washington under executed chain-of-custody.
- Soil cores for SEP analysis will be maintained in the upright position immediately following collection and packaged for shipment in such a way that will preserve this orientation prior to their arrival at the laboratory.
- All soil samples collected for chemical analyses will be and handled in accordance with the QAPP and any applicable revisions.

## 5.0 References

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CH2M HILL. 2005. *Quality Assurance Project Plan (Revised), Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey*. October.

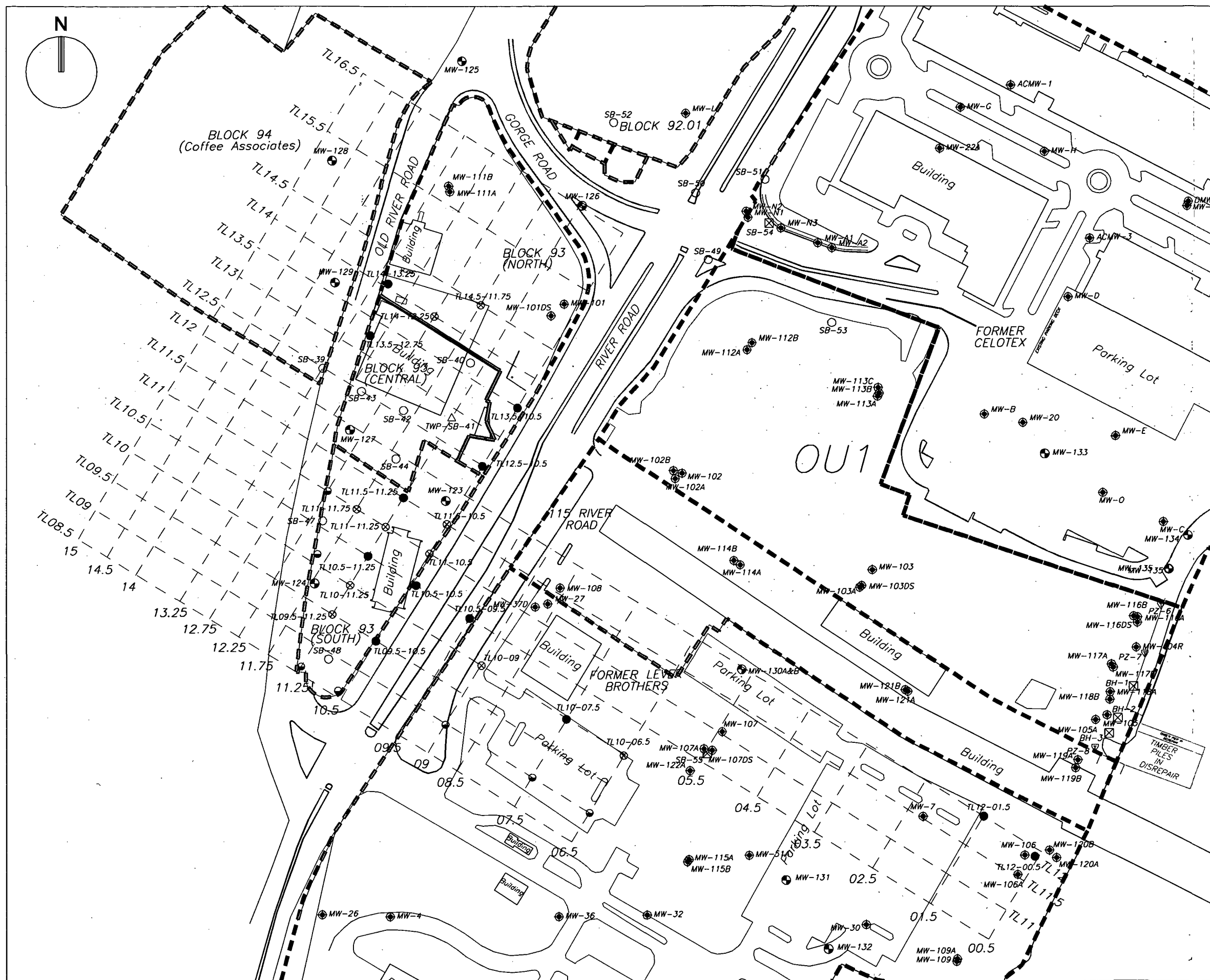
CH2M HILL. 2006a. *Quality Assurance Project Plan (Revised), Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey*. November.

CH2M HILL. 2006b. *Remedial Investigation/Feasibility Study Work Plan Addendum OU1, Quanta Resources Site, Edgewater, New Jersey*. July.

Parsons. 2005. *Field Sampling Plan, Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey*. May.

## Figures

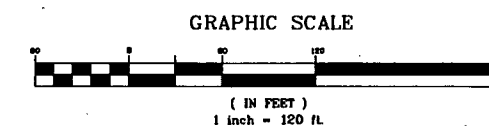
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# LEGEND

- TarGOST™ GRID LINES
- PROPOSED TarGOST™ DIRECT-PUSH VERTICAL PROFILING LOCATION
- PROPOSED TarGOST™ & DIRECT-PUSH SOIL BORING LOCATION
- PROPOSED DIRECT-PUSH SOIL BORING
- PROPOSED DIRECT-PUSH SOIL BORING & GW GRAB LOCATION
- PROPOSED ROTASONIC SOIL BORING
- PROPOSED ROTASONIC BORING SOIL TO BE COMPLETED AS A MONITORING WELL
- PROPOSED ROTASONIC BORING SOIL TO BE COMPLETED AS NESTED PIEZOMETER
- EXISTING MONITORING WELL
- CURRENT PROPERTY BOUNDARY

NOTES:  
1. Depiction of other properties are based on available tax maps and drawings generated by other consultants as part of environmental studies.  
2. Depiction of other properties on this figure is for comparative purposes and does not necessarily suggest that site-related constituents have migrated there.

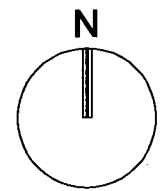
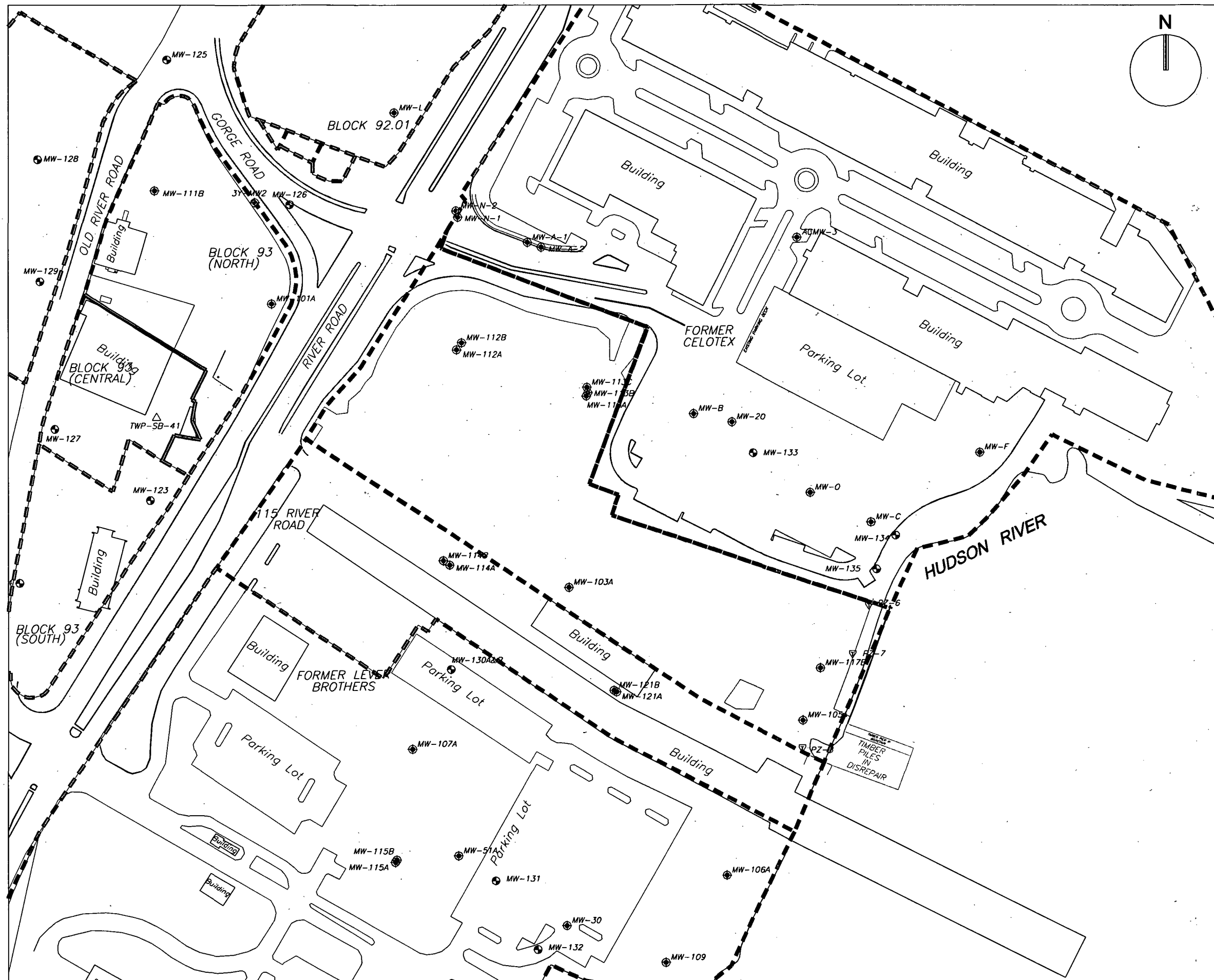


SRI - TarGOST®, SOIL BORING & MONITORING WELL INSTALLATION PLAN

Quanta Resources Superfund Site  
Edgewater, New Jersey

May 14, 2008

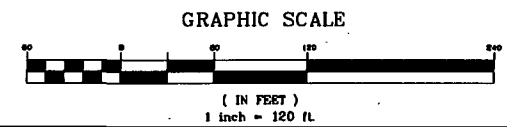
FIGURE B-1



# LEGEND

- EXISTING MONITORING WELL
- PROPOSED MONITORING WELL
- ▽ PROPOSED NESTED PIEZOMETER
- PROPOSED MONITORING WELL LOCATION FOR BOTH 2008 SEMI-ANNUAL GROUNDWATER SAMPLING EVENTS
- PROPOSED MONITORING WELL LOCATION FOR 1ST 2008 SEMI-ANNUAL SAMPLING EVENT ONLY
- ▽ SEMI-ANNUAL DEPTH TO GROUNDWATER AND NAPL GAUGING LOCATION WHERE SAMPLES WILL NOT BE COLLECTED
- △ PROPOSED ONE-TIME GROUNDWATER GRAB SAMPLING LOCATION (NO GEOCHEMICAL PARAMETERS)
- CURRENT PROPERTY BOUNDARY

NOTES:  
1. Depiction of other properties are based on available tax maps and drawings generated by other consultants as part of environmental studies.  
2. Depiction of other properties on this figure is for comparative purposes and does not necessarily suggest that site-related constituents have migrated there.



SRI - PROPOSED 2008 SEMI-ANNUAL GROUNDWATER MONITORING LOCATIONS

Quanta Resources Superfund Site  
Edgewater, New Jersey

March 5, 2008

FIGURE B-2

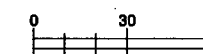


## LEGEND

- QUANTA PROPERTY BOUNDARY
- HUDSON RIVER SHORELINE
- EXISTING GROUNDWATER MONITORING WELL
- POTENTIAL PHASE 1 BOREHOLE VSP SURVEY LOCATION
- POTENTIAL PHASE 2 BOREHOLE VSP SURVEY LOCATION
- APPROXIMATE LOCATION OF PROPOSED PHASE 1 SURFACE GEOPHYSICS

### Basemap Sources:

- a.) Boundary and topographic survey of Block 95, Lot 1 and Block 93, Lots 1, 2, and 3 performed by Vargo Associates in September 2005 and updated as recently as June 2007.
- b.) Borough of Edgewater Tax Map - November, 1959
- c.) Coal Tar Engineering Design Report (Environ, July 2006)
- d.) Site Investigation Report, Part 4 (Langan, May 2004) for the former Lever Bros. Property.



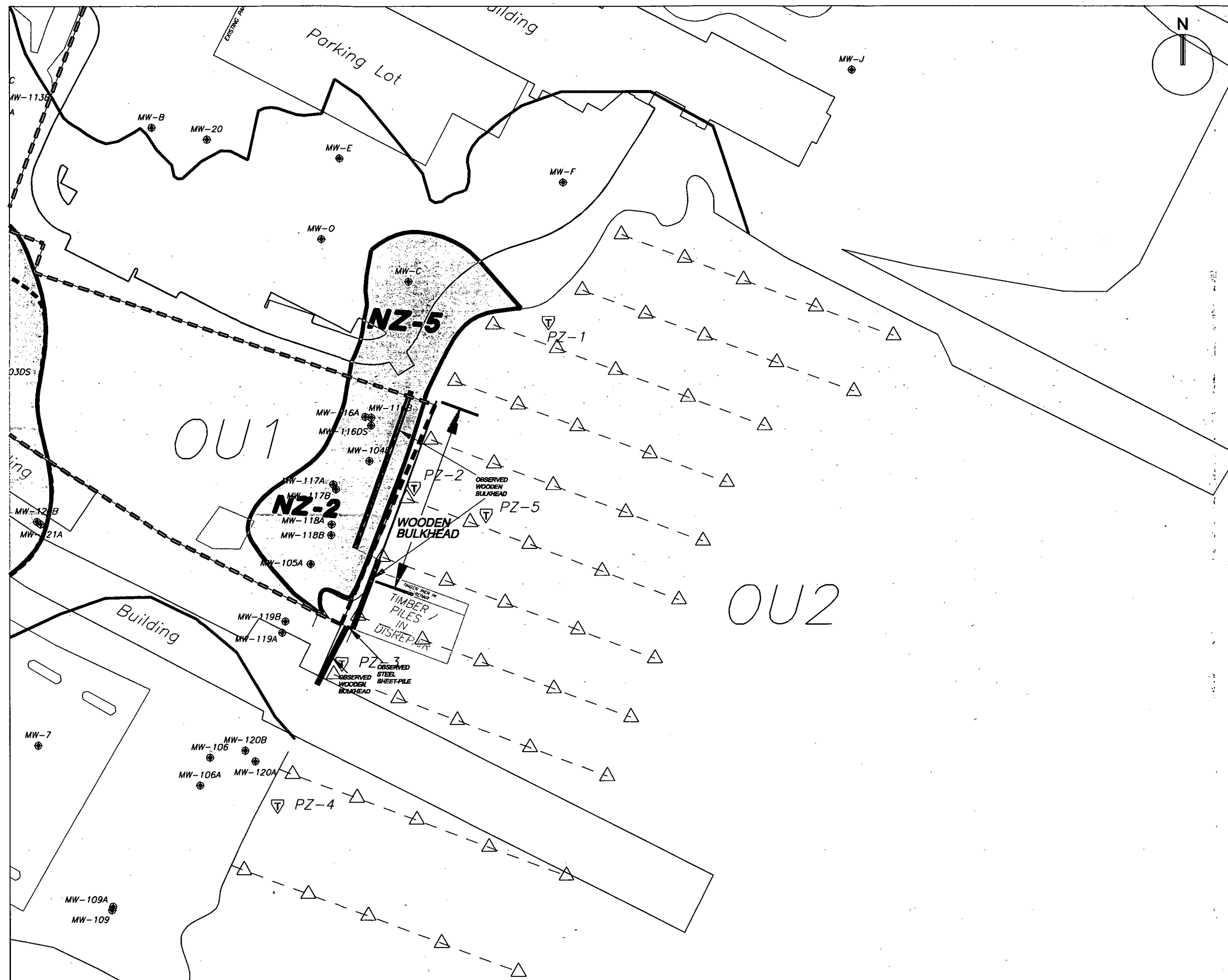
**CH2MHILL**

**SRI - GEOPHYSICAL SURVEY  
LOCATION PLAN**

**Quanta Resources Superfund Site  
Operable Unit 1  
Edgewater, New Jersey**

May 14, 2008

**FIGURE B-3**

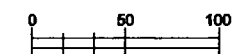


## LEGEND

- QUANTA PROPERTY BOUNDARY
- HUDSON RIVER SHORELINE
- EXTENT OF COAL TAR (INCLUDES NON-AQUEOUS PHASE LIQUID (NAPL), SOLID TARS, AND SOIL IMPACTS)
- NZ-2** KEY NAPL ZONE
- EXISTING GROUNDWATER MONITORING WELL
- △ PROPOSED TRIDENT PROBE LOCATION
- ▽ PROPOSED HAND-DRIVEN NESTED PIEZOMETER - OU2

### Basemap Sources:

- a.) Boundary and topographic survey of Block 95, Lot 1 and Block 93, Lots 1, 2, and 3 performed by Vargo Associates in September 2005 and updated as recently as June 2007.
- b.) Borough of Edgewater Tax Map - November, 1959
- c.) Coal Tar Engineering Design Report (Environ, July 2005)
- d.) Site Investigation Report, Part 4 (Langan, May 2004) for the former Lever Bros. Property.



**CH2MHILL**

**SRI - TRIDENT PROBE SURVEY & OU2 PIEZOMETER INSTALLATION LOCATIONS**

**Quanta Resources Superfund Site  
Operable Unit 1  
Edgewater, New Jersey**

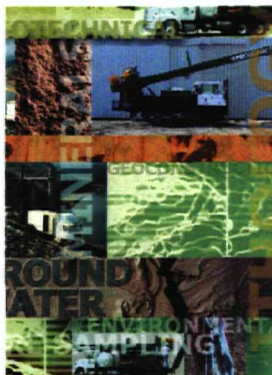
May 14, 2008

**FIGURE B-4**

**Attachment B-1**  
**Information on Multi-case Override**  
**Borehole Isolation Method**

---





## The PROSONIC® Multi-Case Override System

### Penetrate multiple aquifers *without* permanent surface casing

Conventional borehole drilling in contaminated areas runs the risk of facilitating the migration of contaminants from one zone into another. In many documented cases, drilling activities have caused the spread of contamination into zones that were previously considered uncontaminated, either through drilling or through improperly grouted surface well casings.

Consequently, it is standard industry procedure to first grout in a permanent surface casing before penetrating a confining layer or aquitard. This process is time consuming, expensive and doesn't always ensure against creating a pathway for contaminants to travel.

Fortunately, The PROSONIC® Method and the casing override system offer a more effective way - saving time, money and eliminating the potential for cross contamination.

PROSONIC®'s multi-case override system can eliminate permanent surface casings. Alternatively, temporary Sonic casings are used to seal isolated zones, which are then removed upon completion of the borehole and final grouting.

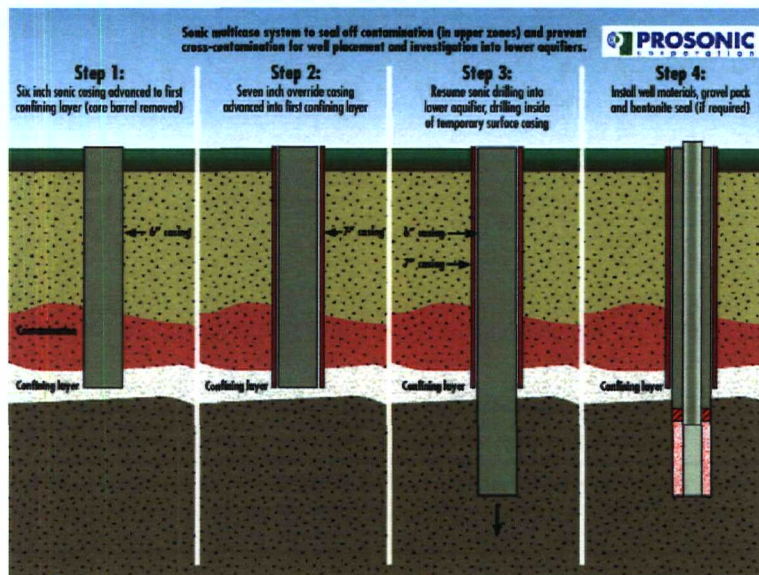


Figure 1

#### Here's why:

The PROSONIC® Method substantially reduces the friction of the soil immediately surrounding the advancing core barrel or casing (one of the keys to the very high penetration rates achieved with The PROSONIC® Method). Once the Sonic energy is stopped, however, the soil re-forms adjacent to the pipe. If this is done within a confining layer, the re-formed soil actually creates a seal against the casing wall.

The PROSONIC® multi-case override system utilizes larger diameter casings that are over-drilled into a confining layer. A smaller diameter drill string is placed inside the temporary surface casing and advanced to depth.

*continued on reverse*



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## The PROSONIC® Multi-Case Override System *continued*

### Here's how:

As an example, suppose a 2-inch monitoring well is to be installed below a confining layer of clay. The four steps outlined below illustrate how PROSONIC®'s multi-case override system works. (Figure 1)

- Step 1. Core and case a six-inch borehole into the confining layer.
- Step 2. Sonically override a seven-inch casing into the confining layer over the six-inch casing completed in step 1. Both casings are then sealed and pressurized with water or air for a period of time to check for leakage. This confirms that a seal exists between the seven-inch temporary casing and surrounding formation.
- Step 3. Resume Sonically coring and casing a six-inch borehole to depth inside of the seven inch casing. No Sonic energy is applied to the seven-inch casing.
- Step 4. Install well materials (screen, riser pipe, gravel pack, seal, and grout).
- Step 5. To complete the process, remove the six- and seven-inch Sonic casings in reverse order (first the six, then the seven-inch) while sonic energy is being applied to the casings. (Figure 2)

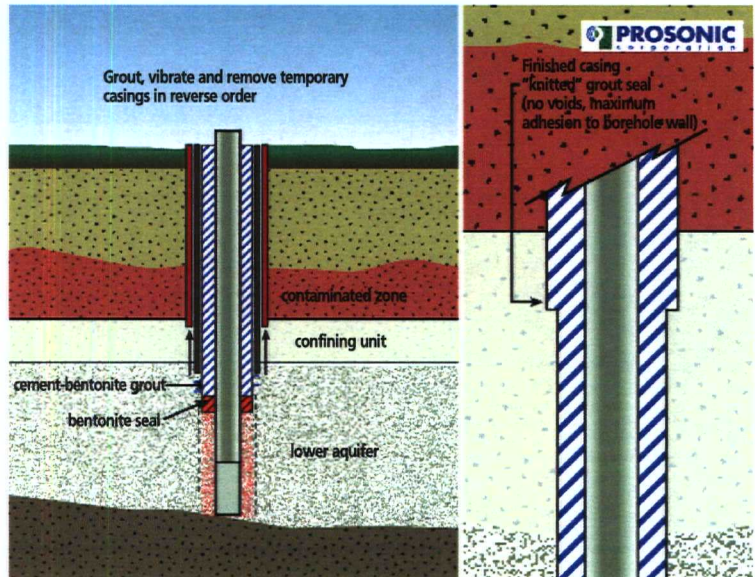


Figure 2

### The end result:

- The installation has been completed in a fraction of the time that would be needed with conventional drilling.
- Fewer materials are used because there is no permanent surface casing required.
- Unlike a permanent surface casing that may not be properly grouted or may deteriorate over time, PROSONIC®'s permanent seal eliminates cross-contamination. A grout collar is "knitted" into the borehole wall through the confining layer.



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Attachment C

**Copy of Sequential Extraction Laboratory  
Analytical Procedure (Wenzel et al.,2000)  
and Details on Method Modifications**

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## **Modifications to Applied Speciation's proposed Sequential Extraction Procedure as described in Wenzel et. al., 2001**

In accordance with the request by CH2M HILL on March 21, 2008 the following is an outline for the fractionation of arsenic in a complex substrate facilitating sequential extraction procedures (SEP). The purpose of the sequential extraction procedure (SEP) is to solubilize specific components of the solid substrate to characterize the fate of arsenic.

The efficacy of each extraction procedure can be impacted by the chemical components of the substrate; thus, the performance of the method is operationally defined. Monitoring ancillary elements for each extraction step can provide insight into the interaction of the individual extraction solutions with the substrate and further elucidate correlations between arsenic and the target fractions. The proposed list of ancillary elements is: Fe, Mg, Ca, Mn, Al, and Si.

All sample handling (including drying) and extractions will occur in an oxygen-free glove box. A five-step SEP will be performed on each individual sample. One-foot long sealed acetate or Lexan® lined sample cores provided to the laboratory will be sub-sampled in such a way that will avoid the inclusion of organic debris (wood, leaves, coal, etc...) as well as larger grained soil particles (> 5 mm in diameter).

The SEP procedure will involve the following five (5) extractions performed in the order presented:

- 1.) A 2-step deionized (DI) water leach will replace the initial  $\text{NH}_4(2\text{SO}_4)$  (ammonium sulfate) extraction. Deionized water leaches will be applied to the sample prior to drying procedure to yield readily dissociable and soluble arsenic (pore water). Both DI leaches will be done with Argon-purged water to remove as much DO as possible (<1 ppm). The pH will be measured and reported on both leachates.
- 2.) An  $(\text{NH}_4)\text{H}_2\text{PO}_4$  (ammonium hydrogen phosphate) leach per Wenzel et. al., 2001 at a pH of 7 to determine specifically-sorbed arsenic [adsorbed outer and inner-sphere complexes. The pH of the resulting leachate will be measured and reported.
- 3.) An  $\text{NH}_4$ -oxalate (ammonium oxalate) buffer leach per Wenzel et. al., 2001 to yield arsenic associated with amorphous and poorly-crystalline hydrous oxides of iron and aluminum.
- 4.) An  $\text{NH}_4$ -oxalate buffer and ascorbic acid leach per Wenzel et. al., 2001 to yield arsenic associated with well-crystallized hydrous oxides of iron and aluminum
- 5.) The final residual arsenic fraction (step 5) will be a  $\text{HF}/\text{HNO}_3/\text{HCl}$  digestion rather than the proposed  $\text{HNO}_3/\text{H}_2\text{O}_2$  digestion. Application of the  $\text{HF}/\text{HNO}_3/\text{HCl}$  digestion will ensure that all remaining compounds in the solid will be solubilized to yield arsenic associated with residual phases (thio-arsenicals and encapsulated).

The proposed method is a modified version of the SEP presented by Wenzel et al:

Wenzel, W., Kirchbaumer, N., Prohaska, T. Arsenic fractionation in soils using an improved sequential extraction procedure. 2001. *Analytica Chimica ACTA*. 436:309-323.



Analytica Chimica Acta 436 (2001) 309–323

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## Arsenic fractionation in soils using an improved sequential extraction procedure

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Received 19 September 2000; received in revised form 1 December 2000; accepted 22 February 2001

### Abstract

Risk assessment of contaminants requires simple, meaningful tools to obtain information on contaminant pools of differential lability and bioavailability in the soil. We developed and tested a sequential extraction procedure (SEP) for As by choosing extraction reagents commonly used for sequential extraction of metals, Se and P. Tests with alternative extractants that have been used in SEPs for P and metals, including  $\text{NH}_4\text{NO}_3$ ,  $\text{NaOAc}$ ,  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , EDTA,  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{F}$ , were shown to either have only low extraction efficiency for As, or to be insufficiently selective or specific for the phases targeted. The final sequence obtained includes the following five extraction steps: (1) 0.05 M  $(\text{NH}_4)_2\text{SO}_4$ , 20°C/4 h; (2) 0.05 M  $\text{NH}_4\text{H}_2\text{PO}_4$ , 20°C/16 h; (3) 0.2 M  $\text{NH}_4^+$ -oxalate buffer in the dark, pH 3.25, 20°C/4 h; (4) 0.2 M  $\text{NH}_4^+$ -oxalate buffer + ascorbic acid, pH 3.25, 96°C/0.5 h; (5)  $\text{HNO}_3/\text{H}_2\text{O}_2$  microwave digestion. Within the inherent limitations of chemical fractionation, these As fractions appear to be primarily associated with (1) non-specifically sorbed; (2) specifically-sorbed; (3) amorphous and poorly-crystalline hydrous oxides of Fe and Al; (4) well-crystallized hydrous oxides of Fe and Al; and (5) residual phases. This interpretation is supported by selectivity and specificity tests on soils and pure mineral phases, and by energy dispersive X-ray microanalysis (EDXMA) of As in selected soils. Partitioning of As among these five fractions in 20 soils was (% medians and ranges): (1) 0.24 (0.02–3.8); (2) 9.5 (2.6–25); (3) 42.3 (12–73); (4) 29.2 (13–39); and (5) 17.5 (1.1–38). The modified SEP is easily adaptable in routine soil analysis, is dependable as indicated by repeatability ( $w \geq 0.98$ ) and recovery tests. This SEP can be useful in predicting the changes in the lability of As in various solid phases as a result of soil remediation or alteration in environmental factors. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Sequential extraction; Arsenic; Soil analysis; Chemical fractionation

### 1. Introduction

The occurrence of inorganic As in drinking water has been identified as a source of risk for human

health even at relatively low concentrations. As a consequence more stringent limits for As in drinking water have been recently proposed. The US EPA has recently proposed to reduce the As limit from 50 to  $5 \mu\text{g As l}^{-1}$  [1]. The European Union through the Directive 98/83/EC [2] has fixed a limit of  $10 \mu\text{g As l}^{-1}$  in drinking water in accordance with the WHO limit [3]. Arsenic contamination may be prevalent at mining

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and industrial sites [4], requiring risk assessment that includes information on the potential mobilization of As in soils.

A relatively simple and well-adopted method to assess trace element pools of differential relative lability in soils is the sequential extraction with reagents of increasing dissolution strength. Ideally, each reagent should be targeting a specific solid phase associated with the trace element of interest. Since the stepwise fractionation cannot be quantitatively delineated, the extracted pools are operationally defined. However, thoroughly optimized sequences, e.g. that for metal cations [5] have provided useful information on relative lability and may facilitate a reasonable degree of specificity and selectivity for the extraction steps used [6]. It has also been shown that plant uptake or toxicity can be related to specific fractions of SEPs [7–10]. In other studies, SEPs were used to monitor the partitioning of and subsequent temporal changes in the lability of added metals [11–13].

While there are a large number of sequential extraction procedures available for metal cations [6], only limited work has been done on oxyanions such as As [14]. Based on the chemical similarity of P and As, modified versions of the Chang and Jackson procedure for P [15] have been adopted for As [10]. The extraction steps include  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{F}$ ,  $\text{NaOH}$  and  $\text{H}_2\text{SO}_4$ . Conforming to the interpretation for P it has been suggested that these extractants would correspondingly represent easily exchangeable, and Al-, Fe- and Ca-associated As [10].

The overall efficiencies for extraction of As by 14 reagents have been found to increase in the order: deionized water  $\sim$  1 M  $\text{NH}_4\text{Cl}$   $\sim$  0.5 M  $\text{NH}_4\text{Ac}$   $\sim$  0.5 M  $\text{NH}_4\text{NO}_3$   $\sim$  0.5 M  $(\text{NH}_4)_2\text{SO}_4$   $<$  0.5 M  $\text{NH}_4\text{F}$   $<$  0.5 M  $\text{NaHCO}_4$   $<$  0.5 M  $(\text{NH}_4\text{N})_2\text{CO}_3$   $<$  0.05 M  $\text{HCl}$   $<$  0.025  $\text{H}_2\text{SO}_4$   $<$  0.5 M  $\text{HCl}$   $<$  0.5 M  $\text{Na}_2\text{CO}_3$   $<$  0.5 M  $\text{KH}_2\text{PO}_4$   $<$  0.5 M  $\text{H}_2\text{SO}_4$   $\sim$  0.1 M  $\text{NaOH}$  [16].

Grubel et al. [17] tested the adaptability of extraction steps from commonly used SEPs in fractionating As and Se using standard minerals and mixtures thereof [17]. They showed that during reductive and oxidative dissolution of As from a certain mineral phase, re-adsorption on other mineral phases as well as subsequent desorption of As in the next extraction step can be a serious limitation for SEPs. Similar observations were reported by others for various metals

[18–20]. These limitations conclusively show the need for the development of a more efficient SEP for As that selectively extracts As bound to soil constituents of varying binding capacity.

The main aim of this study was to develop a SEP for As by modifying the Zeien and Brümmer [5] procedure [5] taking into account the anionic nature of As species in soil. This was achieved by introducing extraction steps obtained from other SEPs in order to target all potential primary chemical forms of As in the soil solid phase. These included components of the Chang and Jackson [15] procedure for P [15], the Sacki and Matsumoto [21] procedure for Se [21] and the Han and Banin [22] approach to extract metal fractions associated with carbonates [22].

## 2. Experimental

### 2.1. Preparation of pure phases

Different synthetic phases were prepared by precipitation of hydrous oxides of Al and Fe. Hydrous oxides of Fe and Al were precipitated using  $\text{NaOH}$  from stock solutions of 1 M  $\text{Al}(\text{NO}_3)_3$  and 1 M  $\text{Fe}(\text{NO}_3)_3$ , respectively [23], excess Na was removed using dialysis. Iron oxide-coated sand was prepared by precipitations of crystalline Fe oxides (mainly hematite) on the surface of quartz sand by raising the temperature of a solution of  $\text{FeCl}_3$  to 550°C [24].

### 2.2. Sampling and characterization of experimental soils

Soil samples were collected from As-contaminated sites in Austria according to genetic horizons, air-dried at ambient temperature, and passed through a 2 mm sieve. Arsenic in the samples was due to both geogenic or anthropogenic sources.

Particle size analysis (sand, silt, clay) of the fraction ( $<2\text{ mm}$ ) was carried out by a combined sieve and pipette technique [25]. Soil pH was measured in 1:2.5 soil:0.01 M  $\text{CaCl}_2$  suspension after 2 h of equilibration using a combined pH electrode [25]. Carbonate content was measured volumetrically according to the principle of Scheibler after dissolution with 10%  $\text{HCl}$  [25]. Total C was measured with an instrumental combustion technique (NA 1500 Carlo-Erba Instruments) [25]. Organic C (OC) was calculated

Table 1  
Initial sequence of extractants

Fraction	Extractant	Extraction conditions	SSR <sup>a</sup>	Wash step
1	NH <sub>4</sub> NO <sub>3</sub> (1 M); pH = 7 <sup>b</sup>	30 min shaking, 20°C	1:25	
2	NaAc/HAc buffer (1 M); pH depending on the carbonate content of the soil <sup>c</sup>	6 h shaking; depending on carbonate content repeated up to three times <sup>c</sup>	1:25	
3	NH <sub>2</sub> OH-HCl (0.1 M) + NH <sub>4</sub> OAc (1 M); pH 6.0 <sup>b</sup>	30 min shaking, 20°C	1:25	NH <sub>4</sub> OAc (1 M); pH 6.0; 10 min shaking; SSR 1:12.5; two times
4	NH <sub>4</sub> -EDTA (Titriplex II) 0.025 M; pH 4.6 <sup>b</sup>	90 min shaking, 20°C	1:25	NH <sub>4</sub> Ac (1 M); pH 4.6; SSR 1:12.5, 10 min
5	NH <sub>4</sub> F (0.5 M); pH 7.0 <sup>d</sup>	1 h shaking	1:50	
6	NH <sub>4</sub> -oxalate buffer (0.2 M); pH 3.25 <sup>c</sup>	4 h shaking in the dark, 20°C	1:25	NH <sub>4</sub> -oxalate (0.2 M); pH 3.25; SSR 1:12.5; 10 min shaking in the dark
7	NH <sub>4</sub> -oxalate buffer (0.2 M); pH 3.25 + ascorbic acid (0.1 M) <sup>c</sup>	30 min in a water basin at 96 ± 3°C in the light	1:25	NH <sub>4</sub> -oxalate (0.2 M); pH 3.25; SSR 1:12.5; 10 min shaking in the dark
8	NH <sub>4</sub> F (0.5 M); pH 7.0 <sup>d</sup>		1:50	
9	KOH (0.5 M)	5 min shaking, 40°C	1:50	
10	HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	Microwave digestion	1:50	

<sup>a</sup> SSR: soil solution ratio.

<sup>b</sup> Zeien and Brümmer [5].

<sup>c</sup> Han and Banin [22].

<sup>d</sup> Chang and Jackson [15].

as the difference between total C and the inorganic carbon content estimated from the carbonate content. The cation exchange capacity (CEC) at natural soil pH was calculated as the sum of Al<sup>3+</sup>, Ca<sup>2+</sup>, Fe<sup>3+</sup>, H<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, and Na<sup>+</sup> extracted by 0.1 M BaCl<sub>2</sub>, and corrected for H<sup>+</sup> due to Al hydrolysis [25]. Amorphous and crystalline Al, Fe and Mn hydroxides were extracted by NH<sub>4</sub><sup>+</sup>-oxalate [26] and by bicarbonate-citrate-dithionite [27]. An estimate of the total As concentrations in the soil samples was measured in the filtrates of an acid digest (65% HNO<sub>3</sub> + 30% H<sub>2</sub>O<sub>2</sub>) using a microwave digestion technique (MLS Mega 240) which yields results comparable to standard procedures using aqua regia [25]. Arsenic was analyzed using an Atomic Absorption Spectrometer (AAS) coupled with a FIAS-400-hydride system (Perkin-Elmer 2100). Al, Fe, Mn, Ca, Mg, Na and Si were analyzed in the same digests using inductively coupled plasma optical emission spectrometry (ICP-AES, Plasmaquant, Zeiss, 100).

### 2.3. Sequential extraction

Soil (1 g) was placed in 50 ml centrifugation tubes and 25 ml of the extraction reagents (chemical grade;

pro analysi; supply: Merck, D-64271 Darmstadt, Germany) were added sequentially. After each extraction step the tube containing the soil and the extractant were centrifuged for 15 min at 1700 × g. Solution entrapped in the remaining soil was collected in subsequent wash steps and combined with the corresponding extract (Table 1). The solution was filtered through 0.45 µm cellulose acetate filter paper in PE-bottles and As concentrations were determined as described above. The residual soil was used for the subsequent extraction steps. All extractions were performed in duplicate. Extracts which could not be analyzed immediately were stored in the freezer (20°C). In selected extracts, we measured pH, major cations and dissolved organic carbon (DOC) using UV absorbance at 254 nm [28].

### 2.4. Statistical treatment

The recovery (accuracy) of the final SEP was evaluated by comparing the sum of the five fractions with a single digestion by aqua regia using linear regression and correlation analysis.

The relative similarities of repeated measurements (precision) of one sample (denoted by *e*) as compared

to the variation between 20 different samples (denoted by  $s$ ) were evaluated by the repeatability index  $W$

$$W = \frac{s^2(s)}{(s^2(s) + s^2(e))/2}$$

where  $s^2(s)$  is the expected value for  $\sigma^2(s)$  and  $s^2(e)$  expected value for  $\sigma^2(e)$ . All calculations were performed with SPSS statistical software package.

### 3. Results and discussion

#### 3.1. Selection and testing of extraction steps of a preliminary SEP

A preliminary 10-step procedure was developed by integrating a method for metal cations [5] and some features from procedures commonly used in SEPs for P [15]. This approach was based on theoretical and practical considerations. In particular, the procedure of Zeien and Brümmer [5] is characterized by a thoroughly selected and tested sequence of extractants of decreasing pH aimed at minimizing adverse interactions (re-adsorption, precipitation) between subsequent extractants. Within the inherent limitation of chemical extraction procedures, there is evidence that the chosen extractants are fairly selective and specific for the targeted major metal pools in soil [6]. pH effects on desorption of anionic As species may be less pronounced than for metals [29], however, adverse precipitation and dissolution reactions of As-carrying soil compounds may be minimized by avoiding large pH changes in subsequent extraction steps [5].

The changes adopted for As SEP were based on the following considerations: because of its geochemical similarity with P, As has been assumed to be associated with similar constituents in the soil, including organically-, Al-, Fe- and Ca-bound fractions [10,16] and sequentially extracted using a modified version [30] of the Chang and Jackson procedure for P [15]. Although using different reagents, all but the Al-bound fractions are addressed in some manner in the Zeien and Brümmer SEP [5] as well. Since preferential association of As with hydrous Al oxides was also likely to occur [29], we modified the Zeien and Brümmer SEP by introducing a  $\text{NH}_4\text{F}$ -extraction step adopted from the modified P SEP [30] to target Al-bound As (Table 1). This step was inserted be-

tween the EDTA and the  $\text{NH}_4$ -oxalate steps because the stability of hydrous Al oxides is, in general, lower than that of hydrous Fe oxides, but higher than that of Mn oxides and organically-bound metals [31]. A second  $\text{NH}_4\text{F}$ -extraction step was introduced after the  $\text{NH}_4$ -oxalate-ascorbic acid step to remove potentially re-adsorbed As before applying KOH. The latter extractant was chosen to target As sulfides, and was placed in the extraction sequence prior to the residual fraction because of their high stability [32] and to avoid a drastic increase of extraction pH in subsequent extraction steps.

This preliminary procedure (Table 1) was tested using four soils (A, B, C, and E) and a sediment (sample D) (Table 2). Fig. 1 depicts the relative partitioning of As and some major elements among the first nine fractions. Fraction 10, the residual, was not included in the figure because of its large pool size for Fe, Al and Si. In general, partitioning of the major elements among the various fraction is in accordance with expectations. It is apparent that As is most prevalent in the  $\text{NH}_4$ -oxalate and the  $\text{NH}_4\text{F}$  steps. Only minor proportions of As were extracted by NaOAc and EDTA, with other reagents virtually not contributing to As fractionation. Accordingly, we eliminated the KOH, second  $\text{NH}_4\text{F}$  and  $\text{NH}_2\text{OH}\cdot\text{HCl}$  steps.

Further evaluation of the remaining steps was based on the following considerations: EDTA extracted between 2 and 7% of As in fractions 1–9 (Fig. 1), but yielding no relation to soil organic matter (SOM). Sorption of As onto humic acids has been found in pure systems, but As sorption decreased at lower ash contents of the humic acids [33]. There is growing evidence that in contrast to P, As is virtually not associated with SOM when in competition with other soil constituents such as hydrous Fe oxides as sorption sites [34]. In fact, As solubility may even be enhanced in organic surface layers in reference to associated mineral horizons [35]. This may be plausibly due to ion competition between arsenate and DOC for sorption sites.

It was apparent from the preliminary SEP tests that most of As in soils and sediment is associated with hydrous oxides solid phases. Therefore, we then tested the first six steps of the SEP on synthetically precipitated hydrous oxides to investigate the relative extractability of Fe and Al (Fig. 2). The relative partitioning of Fe among these fractions is shown for an



Table 2  
Characteristics of the soils used for testing the modified SEP

Soil	Horizon	pH <sub>CaCl2</sub>	CaCO <sub>3</sub> (g kg <sup>-1</sup> )	OC (mmol <sub>e</sub> kg <sup>-1</sup> )	CEC (g kg <sup>-1</sup> )	Al (g kg <sup>-1</sup> ) <sup>a</sup>	Fe (g kg <sup>-1</sup> ) <sup>a</sup>	Fe (g kg <sup>-1</sup> ) <sup>b</sup>	As <sub>tot</sub> (g kg <sup>-1</sup> )
A	A	7.4	281	—	—	—	—	—	12
B	Bw	6.7	3	13.3	117	766	6890	24900	697
C	AE	3.0	0	216	—	2680	5690	—	125
D	Sediment	7.2	702	9	40	—	—	—	500
E	Ah	6.3	22	18	243	—	—	—	73
F	Bw	4.5	19	17.2	14	6370	22639	22638	147
G	Ah	6.8	25	31.5	246	609	9849	9849	248
H	C	6.8	25	19.8	191	1021	16838	16383	255
I	Ah	5.7	41	68.3	233	1814	15219	15219	236
J	BW	4.4	16	14.8	31	3487	23632	23632	279
K	Ah	4.3	0	79.3	183	2410	6710	13400	242
L	Bw	4.2	0	25.2	67	2370	6160	14100	234
M	Bw	7.3	128	24.5	370	1650	3630	24900	2180

<sup>a</sup> NH<sub>4</sub>-oxalate extractable fraction.

<sup>b</sup> Dithionite extractable fraction.

amorphous Fe oxide and a Fe oxide-coated sand, and that of Al for an amorphous Al oxide. The results confirm that NH<sub>4</sub>-oxalate is effective for targeting amorphous oxihydroxides of both Fe and Al [5,26]. It also indicates that the EDTA included in the SEP to extract the organically-bound fraction, is not specific but may dissolve a considerable proportion (up to 20%) of Fe or Al from amorphous hydrous oxides. These findings suggest that As extracted by EDTA from soils (Fig. 1) was primarily derived from hydrous oxides of Fe and Al and not from the organic phases. All other reagents in the sequence extracted only nil amounts of Fe or Al. Likewise, NH<sub>4</sub>F was also ineffective in extracting Al from the hydrous Al oxide (Fig. 2) even though it was introduced to the SEP for this purpose. Arsenic extracted by NH<sub>4</sub>F from soils (Fig. 1) is therefore likely derived from surfaces of hydrous oxides or other soil minerals, possibly relating to the specifically-sorbed fraction.

Based on the preliminary SEP results using soils we also eliminated EDTA from the SEP due to nil amounts of As extracted by EDTA and poor correlation of this fraction with the SOM.

### 3.2. A modified SEP

Based on preliminary SEP test results, a modified SEP was designed employing alternative reagents for extracting surface-bound fractions of As. NH<sub>4</sub>NO<sub>3</sub>

and NaOAc were replaced by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> to extract non-specifically adsorbed As in a single step. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> had<sup>a</sup> been shown to extract As slightly more effective than NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>OAc solutions of equal ionic strength [16], and had also been successfully used to extract exchangeable Se from soils [21]. NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> was selected for the second step to extract specifically-sorbed As from mineral surfaces. Phosphate solutions were found to be efficient in extracting As from different soils [16,36]. In fact, As and P have similar electron configuration and form triprotic acids with similar dissociation constants [37]. At equal concentrations, phosphate in soil outcompetes arsenate for adsorption sites in soils because of smaller size and higher charge density of phosphates [10,38]. It is then reasonable to assume that excess addition of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> would primarily extract specifically-sorbed As, with improved specificity after removal of easily-exchangeable As by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. A similar approach has been chosen for extraction of selenate adsorbed onto iron oxides [21].

In SEPs for As adopted from the Chang and Jackson SEP for P [15], surface-bound fractions are extracted using NaOH (pH 10). We compared NH<sub>4</sub>OH and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> reagents of different ionic strengths and extraction times for their efficiency and specificity to extract As from five selected soils (Fig. 3). Ammonium rather than Na was chosen to maintain NH<sub>4</sub><sup>+</sup> consistently throughout the SEP and to enable direct

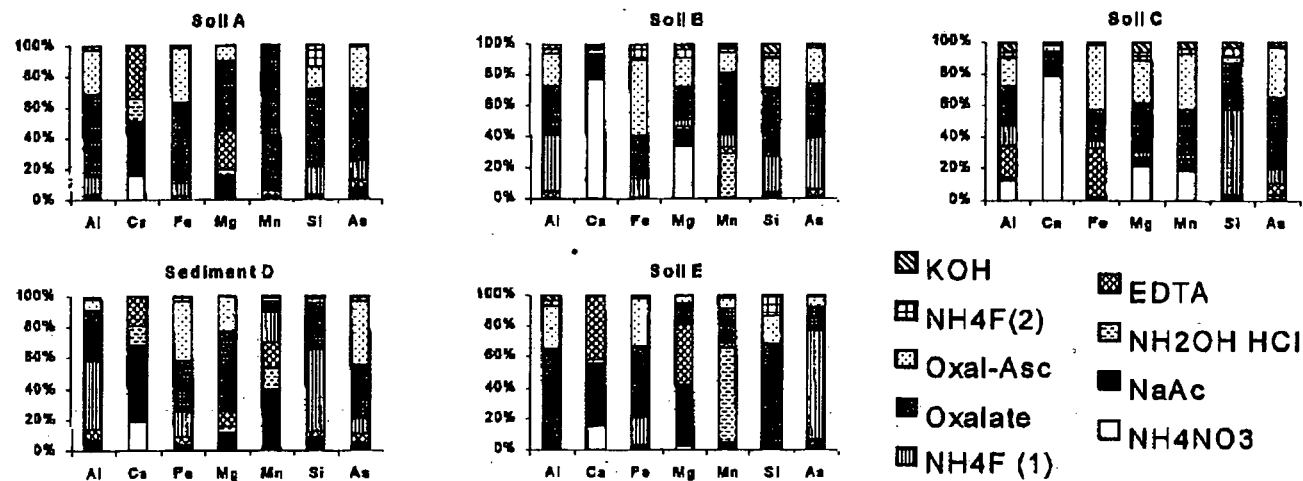


Fig. 1. Partitioning of As and some major elements among the first nine fractions of the preliminary SEP. Characteristics of the soils used are compiled in Table 2, the extraction procedure is described in Table 1.

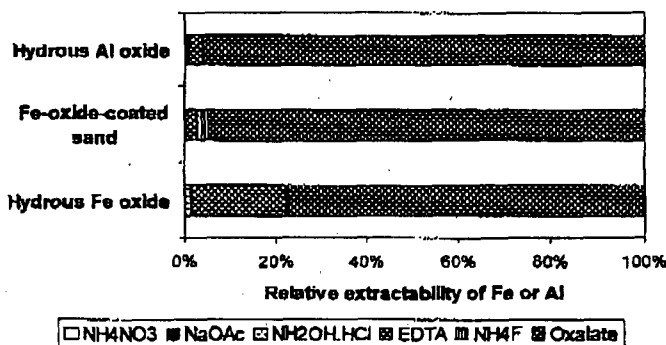


Fig. 2. Partitioning of Fe and Al among the first six fractions of the preliminary SEP (compare Table 1).

comparison with the  $\text{NH}_4\text{H}_2\text{PO}_4$  extraction. The results show that  $\text{NH}_4\text{OH}$  is generally less effective in extracting As (Fig. 3), even though it dissolved considerable amounts of Al and Fe (Table 3) and was expected to extract As more efficiently because of its high pH. Indeed, pH in 0.05 M  $\text{NH}_4\text{OH}$  extracts ranged between 10.4 to 10.9 for the soils (F–J) tested, whereas corresponding pH values in 0.01 M  $\text{CaCl}_2$  and 0.05 M  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  were between 4.3 and 6.8. The unexpected low recovery of As in 0.05 M  $\text{NH}_4\text{OH}$  may be due to re-adsorption of As on fresh surfaces created during the dissolution of hydrous oxides of Al and Fe. Especially in acidic soils,  $\text{NH}_4\text{OH}$  (Table 3) extracted up to about 50% of  $\text{NH}_4$ -oxalate extractable Al (Table 2). It is also notable that  $\text{NH}_4\text{OH}$  dissolved considerably more Al than Fe, invalidating the assumption in the Chang and Jackson procedure [15] that its primary target would have been (surface-bound) Fe-associated forms of P. These particular results concomitant with the high extraction pH inconsistent with the sequence of decreasing pH was the basis for eliminating  $\text{NH}_4\text{OH}$ . In contrast,  $\text{NH}_4\text{H}_2\text{PO}_4$  extracted only small amounts of Al and Fe, indicating its selectivity for surface-bound As fractions.

The extraction efficiency and specificity of  $\text{NH}_4\text{F}$ , compared to 0.05 M  $\text{NH}_4\text{H}_2\text{PO}_4$  were studied using three selected soils (soils K–M, Table 2). Except for soil M, both 0.05 and 0.5 M  $\text{NH}_4\text{F}$  extracts were higher in pH and DOC than  $\text{NH}_4\text{H}_2\text{PO}_4$  extracts (Table 4), with pH increasing as the ionic strength of the extract was increased.  $\text{NH}_4\text{F}$  extraction was also more

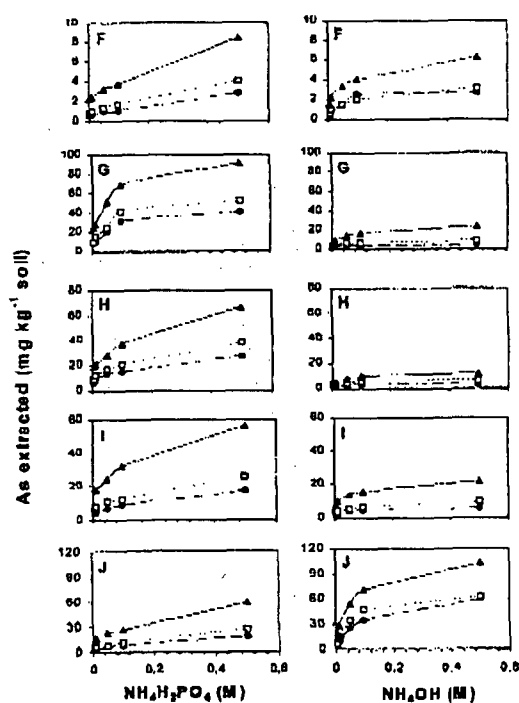


Fig. 3. Extraction of As from soils F–J by  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{NH}_4\text{OH}$  at extractant concentrations between 0.005 and 0.5 M and extraction-times of 0.5 (filled circles), 2 (open squares) and 24 (filled triangles) hours. Extractions were performed at SSR 1:25 and room temperature after removal of easily exchangeable As using 0.05 M  $(\text{NH}_4)_2\text{SO}_4$ . For soil characteristics see Table 2.

Table 3

Extraction of Al and Fe by  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  different extraction times and concentrations<sup>a</sup>

Soil	Extraction time (h)	Extractant concentration (M)	Al ( $\text{mg kg}^{-1}$ )		Fe ( $\text{mg kg}^{-1}$ )	
			$\text{NH}_4\text{OH}$	$\text{NH}_4\text{H}_2\text{PO}_4$	$\text{NH}_4\text{OH}$	$\text{NH}_4\text{H}_2\text{PO}_4$
F	2	0.05	1220	33.4	157	5.50
		0.1	1710	57.0	211	5.76
	24	0.05	1360	34.9	564	13.0
		0.1	1800	47.7	642	7.75
G	2	0.05	59.7	9.46	18.0	5.49
		0.1	54.6	16.2	14.0	9.49
	24	0.05	73.0	11.6	41.2	10.5
		0.1	81.9	17.6	49.2	15.4
H	2	0.05	84.5	8.67	26.1	3.70
		0.1	91.6	15.6	27.7	7.06
	24	0.05	118	10.3	74.6	7.07
		0.1	135	15.3	85.9	10.0
I	2	0.05	299	25.2	85.9	10.9
		0.1	333	45.2	96.2	11.2
	24	0.05	454	31.2	358	25.6
		0.1	553	45.2	426	30.7
J	2	0.05	1300	28.0	569	9.19
		0.1	n.d.	51.2	n.d.	16.4
	24	0.05	1280	41.0	1060	
		0.1	1750	n.d.	1420	n.d.

<sup>a</sup> For soils compare with Table 2.

efficient in extracting Al and Si, while this was not apparent for other major ions and As (Fig. 4). These findings altogether suggest that  $\text{NH}_4\text{F}$  is targeting Al pools that may comprise organically-bound Al as indicated

Table 4

Final pH and DOC and extraction capacity for As of 0.05 M  $(\text{NH}_4)_2\text{SO}_4$ , 0.05 M  $\text{NH}_4\text{H}_2\text{PO}_4$ , 0.05 and 0.5 M  $\text{NH}_4\text{F}$ , respectively<sup>a</sup>

Soil	0.05 M $(\text{NH}_4)_2\text{SO}_4$	0.05 M $\text{NH}_4\text{H}_2\text{PO}_4$	0.05 M $\text{NH}_4\text{F}$	0.5 M $\text{NH}_4\text{F}$
pH				
K	4.53	5.00	6.45	6.80
L	4.33	4.75	6.90	7.30
M	7.60	5.80	6.70	7.50
DOC ( $\text{mg l}^{-1}$ )				
K	39	59	110	104
L	27	50	129	138
M	12	13	17	65
As ( $\text{mg kg}^{-1}$ )				
K	0.5	3.7	5.2	11.3
L	0.3	4.9	9.0	12.8
M	4.0	84.5	27.1	74.2

<sup>a</sup> For soil characteristics see Table 2.

by increased DOC concentrations, and low-order minerals, including allophanes and imogolites as indicated by the concurrent extraction of Si [12]. The concurrent extraction of Al and Si from the acidic soils of this study may also point to hydroxy-Al on external and internal surfaces of micaceous minerals. This specificity of  $\text{NH}_4\text{F}$  for Al is in accordance with the high stability of Al–F complexes [31]. As shown (Fig. 2),  $\text{NH}_4\text{F}$  is virtually not extracting Al from amorphous Al oxides, supporting the hypothesis that extraction would occur primarily from other sources. Even though significant As sorption has been observed on pure minerals [39], and inferred from correlation between acid oxalate-extractable Al and sorption maxima of As in soils [29], it remains questionable if As extracted by  $\text{NH}_4\text{F}$  is directly associated with Al because we found no evidence of As–Al association in EDXMA analysis. This implies that As extraction by  $\text{NH}_4\text{F}$  is not directly linked with the concurrent extraction of Al. Therefore, we decided to eliminate  $\text{NH}_4\text{F}$  from the SEP in view of the above consideration and for its tendency to raise the extraction pH relative to previous extraction steps. Differentiation between Al- and Fe-bound

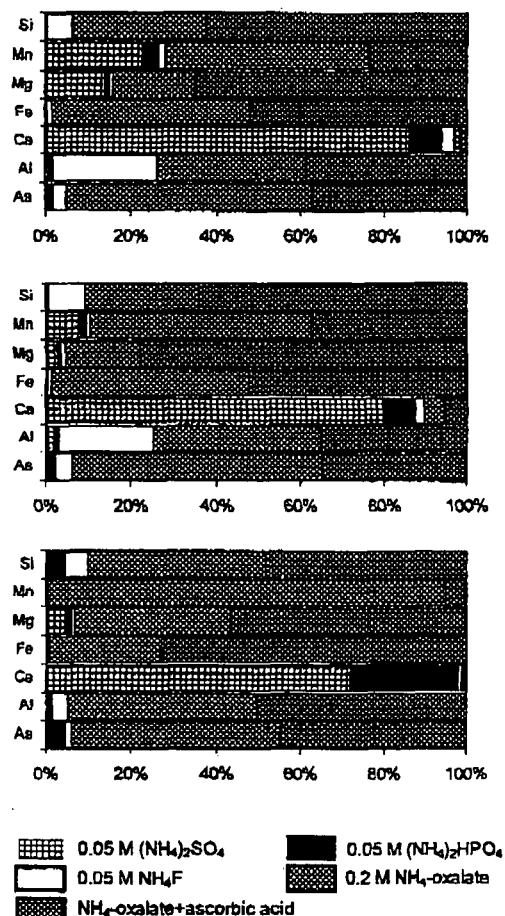


Fig. 4. Extraction capacity for As and major elements of the first six fractions of the modified SEP. For characteristics of soils used see Table 2.

surface species of As using NH<sub>4</sub>F (Al–As) and NaOH (Fe–As) is also complicated by re-adsorption of As during extraction [40]. Moreover, elimination of this step could simplify the procedure for routine purposes without compromising the information needed. However, we recognize that its inclusion may be useful for soils with abundant organically-bound Al and/or imogolite and allophanic minerals such as in volcanic Andisols and some Podisols [12].

A carbonate extraction step using 1 M NaOAc/HOAc buffer solution [22] as described in Table 1 was tested also in the modified SEP prior to the oxalate extraction steps. As indicated by the amount of Ca extracted, this reagent proved to be selective for carbonates, but extracted only negligible amounts of As (data not shown). EDXMA analysis of the same calcareous soils also show that As was not associated with carbonates but primarily bound to hydrous Fe oxides [41]. We conclude that the so-called Ca–As fraction of SEPs based on Chang and Jackson [15] based SEPs [15] is an artifact at least for the soils of our study. We therefore eliminated the NaOAc/HOAc step from the SEP.

### 3.3. Optimization of reagent concentration, extraction time and wash steps for steps 1 and 2

The effect of extractant strength was tested on three different soils using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. Increasing the concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> from 0.005 to 0.5 M had, in spite of a slight decrease of As extractability from soil I, no apparent effect on the amount of As extracted (Fig. 5). In contrast, extracted As increased substantially as the strength of the NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution increased (Fig. 5).

These results infer that (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is extracting a relatively specific fraction of As. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-extractable As is largely independent of the duration and strength of extraction, indicating that this reagent is selective for the non-specifically (easily exchangeable, outer-sphere complexes) fraction of As, whereas, As forms extracted by NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> may represent a suite of surface-bound As species. EXAFS studies of As adsorption on ferrihydrite [42] and goethite [43] have shown the existence of three different inner-sphere surface species of As, including monodentate, bidentate-binuclear and bidentate-mononuclear complexes of different stability and formation kinetics [44,45]. These findings suggest that NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> is extracting varied proportions of these inner-sphere surface complexes of As, depending on the ionic strength of the solution.

Therefore, we selected reagent strengths of 0.05 M for both (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>. From evidence presented above, it appears that (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> may be fairly specific for inner-sphere surface complexes, however, the extraction was apparently

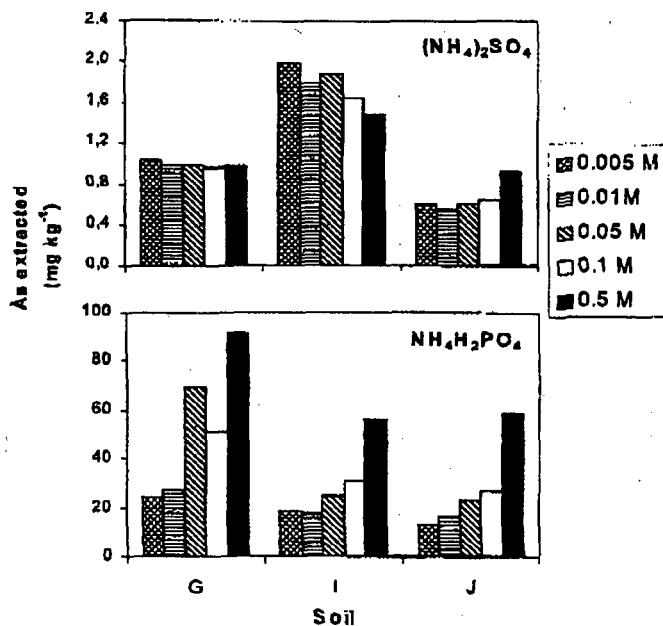


Fig. 5. Extraction capacity after 24 h of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  at extractant concentrations between 0.005 and 0.5 M. Characteristics of soils used (G, I, J) see Table 2.

incomplete and therefore not selective enough even at higher ionic strengths. Since no plateau of extractability at higher ionic strengths was evident from our experiment (Fig. 6), 0.05 M was chosen.

Five soils were used to optimize the extraction time for 0.05 M  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  steps. A plateau was more obtained with  $(\text{NH}_4)_2\text{SO}_4$  after 2 to 5 h (Fig. 6). With  $\text{NH}_4\text{H}_2\text{PO}_4$  a plateau became imminent only after about 10 h (Fig. 6). Based on these results, the extraction times selected were 4 h for  $(\text{NH}_4)_2\text{SO}_4$  and 16 h for  $\text{NH}_4\text{H}_2\text{PO}_4$ . The latter was chosen to allow for convenient overnight shaking of the  $\text{NH}_4\text{H}_2\text{PO}_4$ -step.

To account for potential carry-over to subsequent extraction steps, we tested wash steps to remove As in the solution entrapped in the remaining soil after centrifugation; 10 ml deionized water were added to the remaining soil. After 2 min shaking, the solution was separated and further treated as described for the main extraction steps. The ratio between As extracted

in the wash and main steps at various extraction times are presented in Fig. 7 for 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  and 0.5 M  $\text{NH}_4\text{H}_2\text{PO}_4$  (means and S.D. for five soils). It is apparent that the proportion of As in the wash step for  $(\text{NH}_4)_2\text{SO}_4$  was independent of extraction time, whereas decreased as extraction time was increased in the case of  $\text{NH}_4\text{H}_2\text{PO}_4$ . For an extraction time of 4 h, the wash step extracts  $6.1 \pm 1.5\%$  of the As obtained in the main extraction step. For  $\text{NH}_4\text{H}_2\text{PO}_4$ , the wash step accounts only for  $<2\%$  of the As extracted in the main step. Based on this results we decided to eliminate wash steps for the first two fractions. Considering their substantially larger pool size (see later), subsequent extraction steps would hardly be affected by carry-over of As entrapped in the remaining solution of the previous step. Moreover, at the selected extraction time of 16 h, the selectivity of extraction step 2 remains virtually unchanged if the wash step is omitted. The error is more pronounced for  $(\text{NH}_4)_2\text{SO}_4$ , however, for many (unpolluted) soils

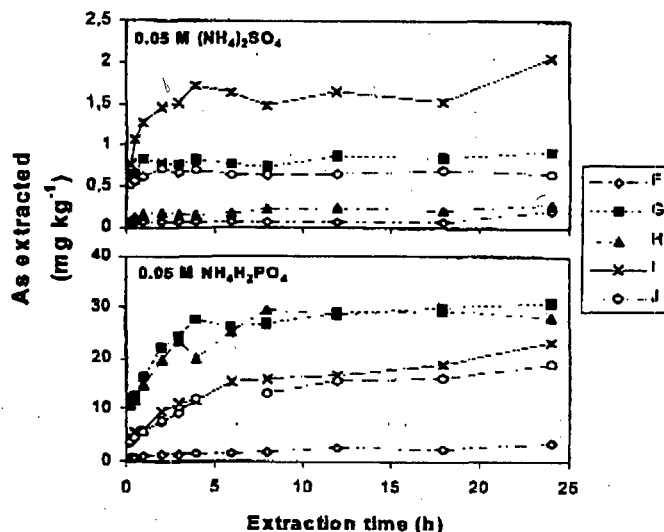


Fig. 6. Extraction capacity for As of 0.05 M  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  solutions as a function of extraction time. For characteristics of soils used (F–J) see Table 2.

dilution to concentrations close to the detection limit of AAS upon combination of main extraction and wash solutions would introduce larger errors. Elimination of the wash steps saves also handling time which is particularly important in routine applications.

### 3.4. Application of the adopted SEP

Twenty soils differing in the level of As contamination ( $96\text{--}2183\text{ mg kg}^{-1}$ ) and soil characteristics (Table 5) were extracted with an adopted five-step SEP (Table 6). These soils are from a spectrum of As-contaminated sites in Austria. The results show that As was most prevalent in the two oxalate fractions, indicating that As is primarily associated with amorphous and crystalline Fe oxides. These findings are in agreement with EDXMA results on selected soils used in this study [41], providing evidence for strong association of As with hydrous Fe oxides whereas primary minerals containing As are generally scarce and limited to arsenopyrite and arsenosiderite. The fraction of As extracted by  $\text{NH}_4\text{H}_2\text{PO}_4$  represented about 10% of total As and may be useful in providing a relative measure of specifically-sorbed As in soils that may be potentially mobilized due to changes in pH or P addition. The amount of readily labile As extracted by  $(\text{NH}_4)_2\text{SO}_4$  is generally small, but may represent the most important fraction related to environmental risks and has been shown to correlate well with As concentrations in field-collected soil solutions [35].

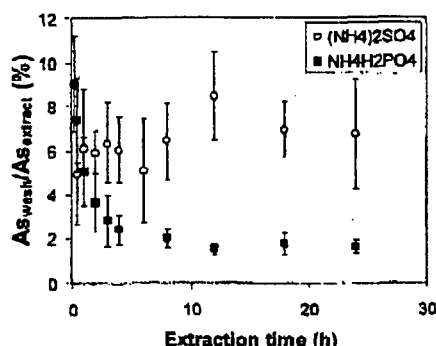


Fig. 7. Ratio between As extracted in wash ( $\text{As}_{\text{wash}}$ ) and main steps ( $\text{As}_{\text{extract}}$ ) for 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  and 0.05 M  $\text{NH}_4\text{H}_2\text{PO}_4$  extractions at various extraction times (%). Symbols represent means of five soils (F–J, compare Table 2), error bars the corresponding standard deviations.

Table 5  
Characteristics of the 20 soils used for testing the final SEP

Property	Unit	Mean	Median	Maximum	Minimum
CaCl <sub>2</sub> pH		5.47	5.73	7.30	2.92
CaCO <sub>3</sub>	g kg <sup>-1</sup>	23	2	181	0
OC	g kg <sup>-1</sup>	44.2	25.8	216	9.74
CFC	mmol c kg <sup>-1</sup>	184	146	475	14.2
Al <sub>e</sub>	g kg <sup>-1</sup>	2.08	1.53	8.03	0.41
Fe <sub>e</sub>	g kg <sup>-1</sup>	5.95	4.92	20.6	2.75
Al <sub>d</sub>	g kg <sup>-1</sup>	2.43	1.83	7.21	0.61
Fe <sub>d</sub>	g kg <sup>-1</sup>	21.4	20.8	34.8	9.85
Sand	g kg <sup>-1</sup>	438	458	670	80
Silt	g kg <sup>-1</sup>	377	328	750	195
Clay	g kg <sup>-1</sup>	185	173	335	65

Fig. 8 provides further evidence that (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>- and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>-extractable As are associated with surfaces of solid phases. Both fractions show a significant ( $P < 0.001$ ) correlation with CEC if the three atypical soils are excluded (Figs. 7 and 8). These soils have unusual high silt but low sand contents. This correlation suggests that As is less strongly adsorbed on the surfaces of minerals when these surfaces display high net negative charges indicated by large CEC.

### 3.5. Appraisal of the SEP

The precision of individual extraction steps was evaluated by calculating the repeatability ( $w$ ) using replicated extraction of the adopted SEP on 20 soils.

We found  $w > 0.98$  for all extraction steps, indicating satisfactory repeatability. Coefficients of variation for replicates were typically below 10% for fractions 1 to 4, and below 20% for the residual fraction. These results indicate reasonable precision of the adopted SEP as compared to other procedures [46].

The accuracy of adopted SEP was tested by comparing the sum of the five fractions ( $As_{sum}$ ) against the total As ( $As_t$ ) concentrations independently measured in a single acid digest (Table 6). The correlation between  $As_{sum}$  and  $As_t$  is highly significant ( $R^2 = 0.95$ ,  $P < 0.0001$ ) for the 20 investigated soils, with  $As_{sum} = 0.88As_t$  (S.E. of intercept = 32.8; S.E. of slope = 0.033). The recovery by the SEP was on the average approximately 12% below that obtained from

Table 6  
Final sequential extraction procedure for As

Fraction	Extractant	Extraction conditions	SSR <sup>a</sup>	Wash step
1	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (0.05 M) <sup>b</sup>	4 h shaking, 20°C	1:25	
2	(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub> (0.05 M) <sup>b</sup>	16 h shaking, 20°C	1:25	
3	NH <sub>4</sub> -oxalate buffer (0.2 M); pH 3.25 <sup>c</sup>	4 h shaking in the dark, 20°C	1:25	NH <sub>4</sub> -oxalate (0.2 M); pH 3.25 SSR 1:12.5; 10 min shaking in the dark
4	NH <sub>4</sub> -oxalate buffer (0.2 M); + ascorbic acid (0.1 M) <sup>c</sup> pH 3.25	30 min in a water bath at 96 ± 3°C in the light	1:25	NH <sub>4</sub> -oxalate (0.2 M); pH 3.25 SSR 1:12.5; 10 min shaking in the dark
5	HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	Microwave digestion	1:50 <sup>d</sup>	

<sup>a</sup> SSR: soil solution ratio.

<sup>b</sup> Modified according to Saeki and Matsumoto [21].

<sup>c</sup> Zeien and Brümmer [5].

<sup>d</sup> After the digestion.

1:25 = ? : 40

ammonium sulfate  
ammonium hydrogen phosphate  
ammonium oxalate  
~~ammonium~~ ascorbic acid.

H<sub>2</sub>F<sub>4</sub>/HNO<sub>3</sub>



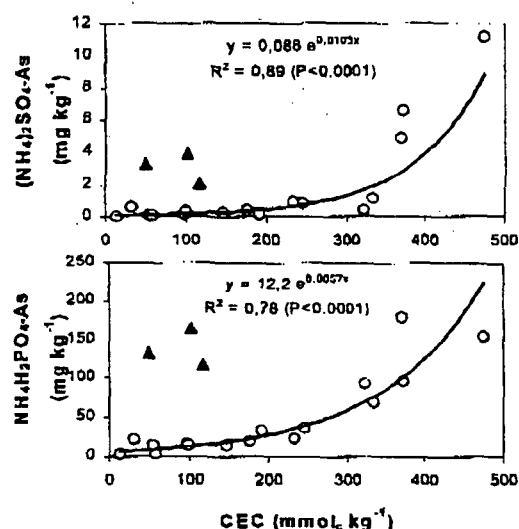


Fig. 8. Exponential relations between CEC and As extractable by 0.05 M  $(\text{NH}_4)_2\text{SO}_4$  and 0.05 M  $\text{NH}_4\text{H}_2\text{PO}_4$ . Soils included in the correlation analyses ( $n = 16$ ) are represented by open circles. Filled triangles designate soils that were excluded from the correlation because of unusual high silt ( $>600 \text{ g kg}^{-1}$ ) and low sand content ( $<150 \text{ g kg}^{-1}$ ).

the total digest, still considered satisfactory. One reason for this underestimation may be the relatively low centrifugation speed ( $1700 \times g$ ) used, which may have caused incomplete sedimentation of humus and clay particles and some loss of the associated As in the subsequent filtration step ( $0.45 \mu\text{m}$ ) in each fraction. It is recommended to choose higher centrifugation speed (e.g.  $3000 \times g$ ) to further improve precision and recovery [47]. Based on their testing of the BCR three-stage SEP for trace metals, Sahuquillo et al. [47] also rec-

ommended to avoid filtration as it may promote dissolution of non-target phases.

Re-adsorption of As on remaining mineral phases during extraction may be a major limitation for any SEP [17,18,20]. Apparently, this problem was minimized in the first two steps of the adopted SEP, since neither  $(\text{NH}_4)_2\text{SO}_4$  nor  $\text{NH}_4\text{H}_2\text{PO}_4$  caused significant dissolution of mineral phases. This is evident from the nil amounts of major cations dissolved by these extraction steps (Fig. 4). However, this problem requires more attention in the case of the two subsequent extraction steps targeting amorphous and crystalline forms of hydrous Fe oxides. In using acidified 0.25 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  ( $\text{pH} < 1$ ) to extract As associated with amorphous hydrous Fe oxides, recovery of As was largely reduced in the presence of goethite, indicating re-adsorption on goethite surfaces [17]. In using 0.2 M  $\text{NH}_4$ -oxalate ( $\text{pH} 3.25$ ) in our SEP, oxalate ions would have competed more effectively with P for adsorption sites [48] than did acid  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . Given the excess concentration of oxalate present during extraction, re-adsorption of As is likely minimized. In our SEP, a wash step using the same reagent is employed to recover As remaining in the rest solution and re-adsorbed onto soil minerals (Table 7). For eight soils, we measured the wash solutions separately and found, on the average, about 11% of the amount of As extracted in the respective main extraction step 3. In a similar manner, we tested the recovery of As in the wash step after extraction of As using a mixture of  $\text{NH}_4$ -oxalate and ascorbic acid (step 4), targeting As associated with crystalline Fe oxides. On the average, As from this wash step represented 23% of that dissolved in the corresponding main extraction step. Grubel et al. [17] found only small re-adsorption of As on montmorillonite [17]. Accordingly, re-adsorption of As onto clay minerals and other

Table 7  
Partitioning of As among the five fractions of the final SEP in 20 soils<sup>a</sup> in  $\text{mg kg}^{-1}$

	$(\text{NH}_4)_2\text{SO}_4$	$\text{NH}_4\text{H}_2\text{PO}_4$	$\text{NH}_4$ -oxalate	$\text{NH}_4$ -oxalate + ascorbic acid	Residual	Sum of fractions 1–5	Total As
Mean	2.02	61.1	205	186	145	600	683
Median	0.71	28.7	127	60.8	41.0	215	259
Maximum	11.1	180	696	614	688	2182	2183
Minimum	0.02	3.10	25.1	22.9	2.26	73.7	96.7

<sup>a</sup> For characteristics of the soils used and details of the extraction procedure see Table 6. The sum of the five fractions is compared to the total As determined by acid digestion using a microwave technique.

silicates remaining in the soil after removal of the hydrous Fe oxides should be less important. This was revealed by the low desorption of As by a subsequent  $\text{NH}_4\text{F}$  extraction deemed to recover re-adsorbed As fractions in the preliminary procedure (Fig. 1).

#### 4. Conclusion

The adopted SEP presented here provides more dependable information on five fractions of As in soils. These operationally defined fractions can represent non-specifically-bound, specifically-bound, amorphous hydrous oxide-bound, crystalline hydrous oxide-bound and the residual. Within the inherent limitations of chemical fractionation, the reagents of the adopted SEP are fairly specific and selective for these forms of As.

The adopted SEP is simple to execute in routine soil analysis and targets the most abundant environmentally important forms of As. Fraction 1, employed as single extractant, has been shown to correlate well with As in field-collected soil solutions and hence can be used for predicting solute As [35]. Such information is useful in risk assessment of As leaching to the groundwater and of the readily bioavailable fraction. Fractions 2–4 may provide information on potential lability of As from different solid phases as a result of soil remediation or alteration in soil (e.g. redox, pH) and environmental factors.

#### Acknowledgements

This study was supported by the Austrian Federal Ministry (AFM) for Science and Traffic, the AFM for Environment and Family, and the Austrian Federal States Kärnten, Salzburg, and Tirol. IACR-Rothamsted receives grant-aided support from the Biotechnology and Biological Sciences Research Council of the United Kingdom. We are indebted to Dr. Ravi Naidu and Dr. Euan Smith, CSIRO Land & Water, Adelaide, for their careful reading of the manuscript and helpful discussion.

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Attachment D

**Trident Probe - Hardware Description,  
Protocols and Procedures (SPAWAR, 2003)**

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Technical Report 1902  
June 2003

# **Coastal Contaminant Migration Monitoring: The Trident Probe and UltraSeep System**

**Hardware Description, Protocols,  
and Procedures**

**SSC San Diego**

**Computer Sciences Corporation**

**Naval Facilities Engineering  
Services Center**

**Cornell University/Suffolk  
County Health Services**

**Cornell Cooperative Extension  
of Suffolk County**

Approved for public release;  
distribution is unlimited.



**SSC San Diego**  
San Diego, CA 92152-5001

## Executive Summary

Coastal landfills and hazardous waste sites pose a potential environmental threat to surface water bodies through the exchange of groundwater-borne contaminants. Because of this potential threat, there is a general requirement to determine if contaminants from these sites are migrating into marine systems at levels that could pose a threat to the environment.

Increasingly, groundwater is recognized as a potentially significant, although poorly quantified, source of nutrients and contaminant materials to coastal ecosystems. Interest in quantifying the exchange between groundwater seepage and overlying surface water has increased due to potential impacts resulting from anthropogenic land uses. Groundwater discharge originates inland and carries with it contaminants or nutrients, dissolved or colloidal, that could impact the chemical budget of surface-water ecosystems. Previous studies clearly show that groundwater discharge into surface-water environments can significantly contribute to the water budget. This chemical and physical impact may be heightened in smaller bodies of water such as embayments or lagoons, due to their limited volume and restricted fluid exchange with the open ocean.

A collaborative effort between the Environmental Sciences Laboratory at Space and Naval Warfare Systems Center, San Diego (SSC San Diego), the Naval Facilities Engineering Service Center (NFESC), and Cornell Cooperative Extension Marine Program was made to develop improved methods for (1) identifying the spatial location where exchange is likely to take place, and (2) accurately measuring the groundwater seepage across the sediment-water interface. This effort resulted in the development of the Trident probe and the UltraSeep system.

The Trident probe is a simple, direct-push system equipped with temperature, conductivity, and water sampling probes. A measured contrast in temperature and/or conductivity between surface water and groundwater can be used to determine potential areas of groundwater impingement into the surface water. The water-sampling probe is used to collect in situ water samples for detailed chemical characterization of contaminants.

Once potential areas of groundwater impingement are identified, the UltraSeep Meter can be used to make continuous, direct measurements of the groundwater seepage rate using an ultrasonic flow meter. The UltraSeep system also contains a multi-sample, water-sampling system that can pump water to six sequential sampling bags mounted around the perimeter of the meter. Conductivity, temperature, and pressure sensors are also mounted on the unit.

In this document, the initial hardware development, testing, and field protocols are described for new techniques used to identify potential areas of groundwater impingement into surface waters (the Trident probe), as well as techniques for quantifying the flow rates and contaminant levels of groundwater at the surface-water interface (the UltraSeep System).

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## INTRODUCTION

Coastal landfills and hazardous waste sites pose a potential environmental threat to surface water bodies through the exchange of groundwater-borne contaminants. Many of these sites are located adjacent to harbors, bays, estuaries, wetlands, and other coastal environments. Because of this potential threat, there is a general requirement to determine if contaminants from these sites are migrating into marine systems at levels that could pose a threat to the environment.

Increasingly, groundwater is recognized as a potentially significant, although poorly quantified, source of nutrients and contaminant materials to coastal ecosystems. Groundwater discharge (seepage) into coastal and surface-water environments has been studied extensively using various methods (Lee, 1977; Lee and Cherry, 1978; Taniguchi and Fukuo, 1993; Cable et al., 1996; Moore, 1999; Li et al., 1999; Chadwick et al., 1999; Paulsen et al., 2001; Simmons, 1992; Moore, 1996; Valiela and D'Elia, 1990; Montlucon and Sanudo-Wilhelmy, 2000). The primary driver for seepage in near-shore environments is probably the discharge from land to surface water induced by the hydraulic gradient in the terrestrial aquifer. However, significant contribution to seepage may also derive from groundwater circulation and oscillating flow induced by tidal stage (Simmons, 1992; Li et al., 1999). In coastal areas with strong tides, tidal mixing zones may form from the movement of seawater into the aquifer (Figure 1). This tidally mixed zone can be important in controlling the exchange of groundwater due to a process called tidal pumping (Moore, 1996). Tidal pumping is when seawater mixes with groundwater at high tide, and then as the tide recedes, the mixture of seawater and groundwater is drawn out into the coastal waters. Because this process repeats every tidal cycle, appreciable volumes of groundwater can be extracted over time (Moore, 1996; Valiela and D'Elia, 1990).

Interest in quantifying the exchange between seepage and overlying surface water has increased due to potential impacts resulting from anthropogenic land uses. As mentioned above, groundwater discharge originates inland and carries with it contaminants or nutrients, dissolved or colloidal, that could impact the chemical budget of surface-water ecosystems. For example, Montlucon and Sanudo-Wilhelmy (2000) concluded that groundwater discharge into Flanders Bay on Long Island, NY, accounts for up to 37% of the copper distribution in the bay. They also estimated that seepage accounts for approximately 40% of the total river inputs in a study area in the South Atlantic Bight. These studies clearly show that groundwater discharge into surface-water environments can significantly contribute to the water budget. This chemical and physical impact may be heightened in smaller bodies of water such as embayments or lagoons, due to their limited volume and restricted fluid exchange with the open ocean.

Several measurement techniques have been proposed and implemented over the past 25 years. Lee (1977) made the first breakthrough in quantifying seepage into surface waters. This breakthrough involves a device consisting of a cut-off section of a 55-gallon drum (area,  $0.255 \text{ m}^2$ ) in which the open-end is inserted into the sediment. Attached to the drum via an outflow port is a 4-l plastic bag that collects the seepage. The volume of the bag and sampling interval are recorded and the specific discharge is obtained by dividing

the volume of collected seepage by the area of the drum. Although generally quite effective, various errors associated with the device must be corrected before sampling (Shaw and Prepas, 1989; Belanger and Montgomery, 1992). Another disadvantage to this method is that it is quite labor-intensive because the plastic bags must be monitored and replaced continuously.

Cherkauer and McBride (1988) overcame some of these shortcomings by designing a remotely operated seepage meter. Plastic collection bags were used, but separate chambers were installed so that samples could be collected remotely. This meter did not require manual installation, but it was heavy enough to sink into the bottom sediment as it was lowered. The major drawback to this seepage meter was that with a weight of greater than 150 pounds, it was not very portable, could only be used in large water bodies, and might distort flow paths slightly as it was sealed into the bottom.

Further advancement of the Lee (1977) technique came from Chadwick et al. (1999). Their meter consists of six chambers capable of automated measurements. Attached to each chamber is a plastic collection bag that collects seepage over a specified time interval. Seepage is collected until all six chambers have taken measurements.

A major advance in quantifying transient seepage came from Taniguchi and Fukuo (1993). Their seepage meter is based on a thermal perturbation technique and can continuously record specific discharge. Although divers are still needed, the deployment and measurement of seepage is much less labor-intensive than previous methods. Another method used by McIlvaine (1998) infers groundwater discharge across the sediment-water interface through pressure gradients using the Portable In-Situ Pore Pressure Instrument II (PISPPi). The pressure gradients are recorded during the recovery of a negative pressure pulse that is generated using a hand-held pump connected to the probe of the instrument. This instrument can also measure the hydraulic conductivity of the sediment.

Building on these historical advances, a collaborative effort between the Environmental Sciences Laboratory at Space and Naval Warfare Systems Center, San Diego (SSC San Diego) and Cornell Cooperative Extension Marine Program set out to develop improved methods for (1) identifying the spatial location where exchange is likely to take place, and (2) accurately measuring the groundwater seepage across the sediment-water interface. In this document, we describe the initial hardware development, testing, and field protocols for new techniques for identifying potential areas of groundwater impingement into surface waters (the Trident probe), as well as techniques for quantifying the flow rates and contaminant levels of groundwater at the surface-water interface (the UltraSeep System).

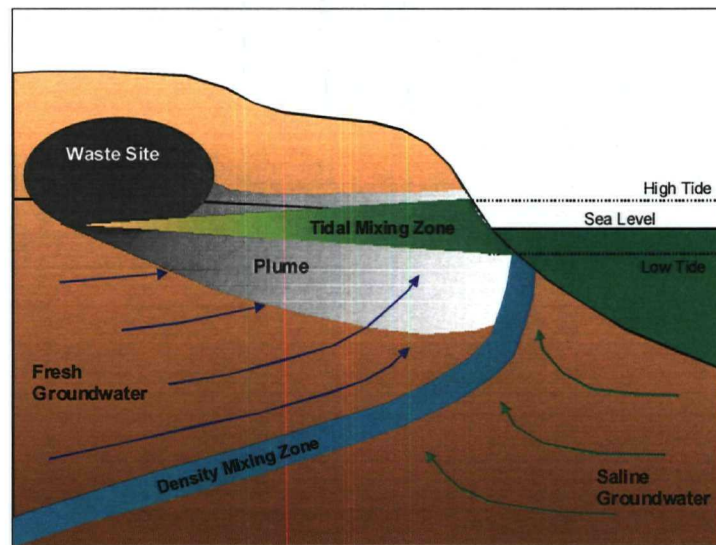


Figure 1. Conceptual representation of coastal contaminant migration process and associated groundwater-surface water interaction.

## HARDWARE DESCRIPTION

### The Trident Probe

To identify potential areas where groundwater is entering the surface water, we have developed the Trident Probe (Figure 2), a simple direct-push system equipped with temperature, conductivity, and water-sampling probes. Contrasts in temperature and conductivity between surface water and groundwater are used to determine likely areas of groundwater impingement. The water-sampling probe can then be used to collect samples for detailed chemical characterization of contaminants.

The temperature sensor consists of a customized Sea-Bird Electronics, Inc. SBE 38 digital oceanographic thermometer with a ruggedized, 60-cm long titanium probe. The sensor has a measurement range of -5 to +35 °C at an accuracy of 0.001 °C, and a resolution of 0.00025 °C. The sensor response time is about 500 milliseconds. The sensor housing is titanium, with a depth rating of 10,000 meters. Real-time temperature data are transmitted from the unit in ASCII format via RS-232 at a frequency of about 2 Hz. Areas of groundwater seepage may appear either as warm or cold contrast to the surface water, depending on the seasonal and site characteristics.

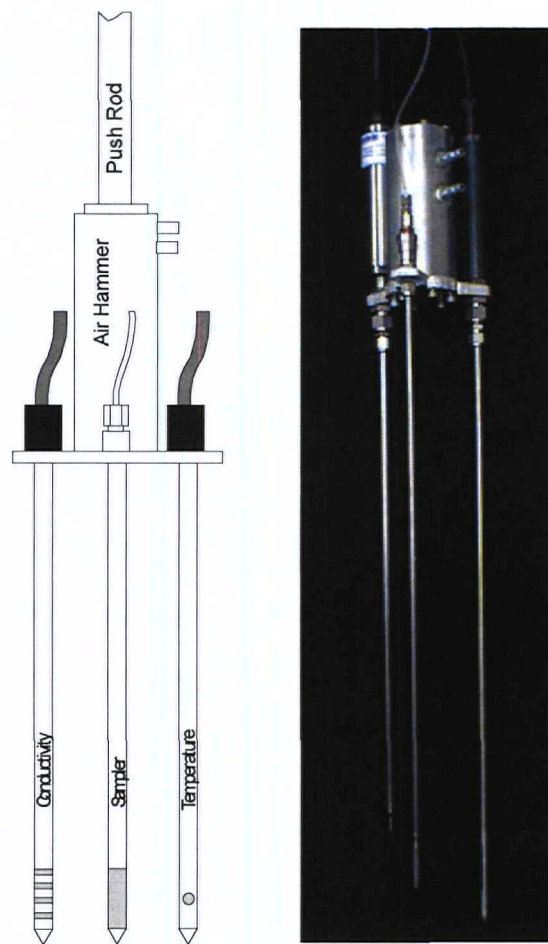


Figure 2. Schematic and photo of Trident probe, showing conductivity, temperature, and water-sampling probes.

The conductivity sensor uses a custom, small-diameter, stainless-steel, Wenner-type probe, 60-cm long. The probe is configured with two pairs of stainless-steel electrodes. A constant current is imposed through the outer pair, and the voltage is monitored through the inner pair. Both pairs of electrodes are coupled through an underwater connector and cable to a standard Geoprobe® model FC4000 deck unit that controls the outer electrode pair current, monitors the inner electrode pair voltage, and sends the corresponding raw conductivity signal to a laptop computer via an RS-232 port. The laptop applies calibration and temperature corrections to the signal, and records and displays the results. The conductivity signal varies primarily as a function of changes in salinity, and secondarily, as a function of clay content and porosity (Figure 3). Areas of likely groundwater seepage are generally associated with low conductivity, either as a result of low salinity, low clay content (high permeability), or both.

The water-sampling probe allows interstitial waters to be extracted from the sediment at selected depths up to about 60 cm below the sediment-water interface. Porewater is

collected by syringe or vacuum pump extraction through a small-diameter, Teflon<sup>®</sup>-coated, stainless-steel probe (see Figure 2). The probes are 1/4-inch-diameter, stainless-steel tubing fitted with a solid point. On the side of the tube near the tip, there is a sample port consisting of a slot covered by a small mesh size (241- $\mu$ m), stainless-steel screen.

The three probes are collocated in a triangular pattern, with a spacing of about 10 cm on an aluminum mounting base. Coupled to the mounting base is a submersible air hammer that assists in driving the probe into the sediment. On the top of the air hammer is a coupling for a 2-m aluminum push rod that can be sequentially lengthened in 2-m increments to a total length of about 10 m. A bundled cable including the temperature and conductivity signals, Teflon<sup>®</sup> sampling tube, and pneumatic air hammer hose runs from the probe to the surface. The sensor signals from the temperature probe and the conductivity deck unit are linked to a laptop computer with real-time display via a graphical MATLAB<sup>®</sup> interface. The Global Positioning System (GPS) is also coupled to the laptop to simultaneously record the sampling locations.

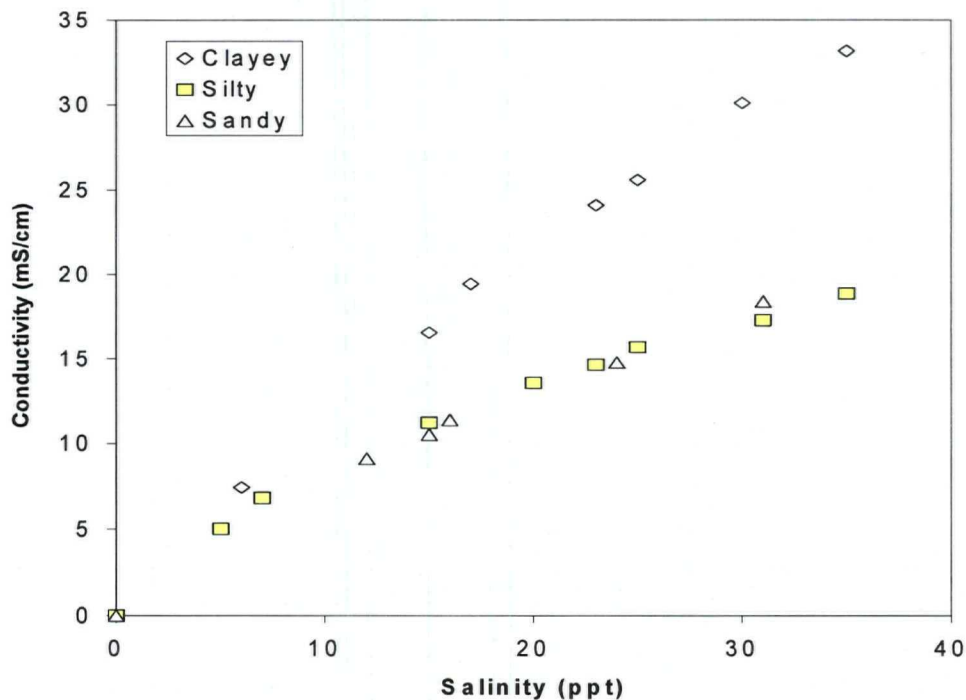


Figure 3. Response of Trident conductivity probe to changes in salinity and sediment type.



In operation, the Trident probe can be deployed in several ways, depending primarily on the depth of the site. In very shallow water (0 to 1 m), the operator simply walks or wades to the sampling station and manually pushes the probe to the desired depth. Experience has shown that the probe pushes easily by hand to a depth of about 30 cm. The air hammer, or a slide hammer, can then complete the push, if necessary. In water of moderate depths (1 to 10 m), the probe is easily deployed from a small boat using the push rod in combination with the air hammer (Figure 4). It is important that the boat be well-anchored to minimize lateral loading on the probe during the insertion. In deeper water (>10 m), a diver can deploy the probe (Figure 5), or it can be attached to a landing frame.

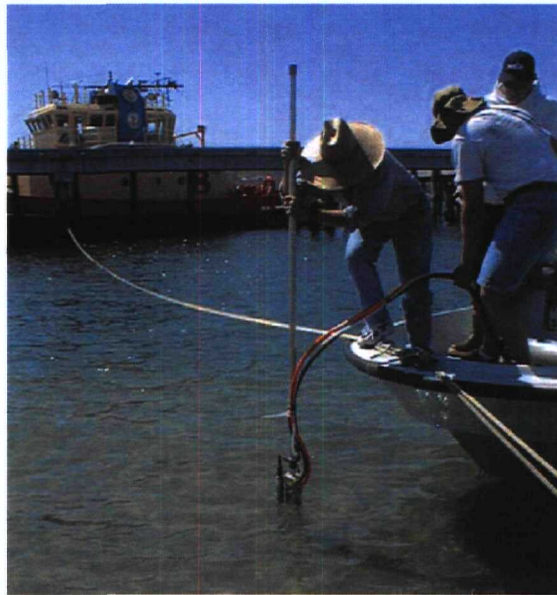


Figure 4. Deployment of Trident probe from small boat using push rod and air hammer.



Figure 5. Diver using air hammer to deploy Trident probe.

### The UltraSeep Meter

The UltraSeep Meter combines the continuous, direct measurement of groundwater seepage rates using the time-transient ultrasonic technique described by Paulsen et al. (2001) with a multi-sample, water-sampling system similar to that described by Chadwick et al. (1999). The meter relies on a Teflon<sup>®</sup>-coated, stainless-steel, open-bottomed chamber measuring 48 x 46 cm to funnel the seepage water to the flow sensor. The flow sensor is connected to the high point of the funnel via 12-mm Teflon<sup>®</sup> tubing, allowing free flow of water between the funnel and the outside environment. A W.S. Ocean Systems (now EnviroTech) ESM data logger/controller unit monitors data from the flow meter. Based on the measured flow conditions, the ESM activates a water-sampling system that can pump water to six sequential sampling bags mounted around the perimeter of the meter. The ESM also records data from conductivity, temperature, and pressure sensors mounted on the unit. All these components, along with a 12-V submersible battery housing, are mounted within a 74-cm-diameter by 79-cm high cylindrical aluminum frame (Figure 6).

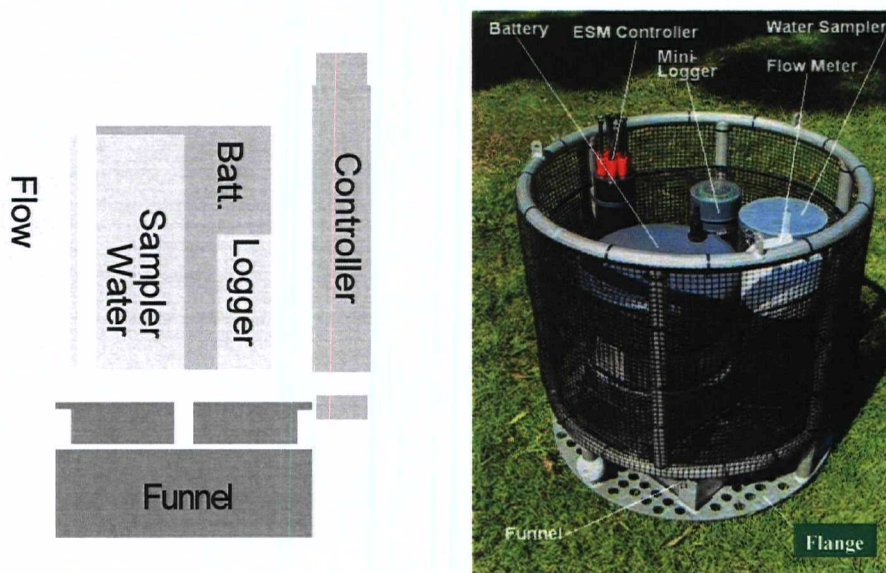


Figure 6. Side view schematic and photo of UltraSeep system.

The ultrasonic flow sensor uses two piezoelectric transducers to continuously measure the travel times of ultrasonic waves along the flow path of the seepage water through the flow tube. As water enters the flow tube, it passes through the ultrasonic beam path. The ultrasonic signal that travels with the flow has a shorter travel time than the signal traveling against flow. The perturbation of travel time is directly proportional to the velocity of flow in the tube. The flow sensor sensitivity is about 1.5 cm<sup>3</sup>/min, which, given the amplification from the funnel, translates to a seepage rate of less than 1 cm/d. Signal averaging can improve this sensitivity further. A Teflon<sup>®</sup>, electrically activated solenoid valve connected in line with the flow tube easily establishes the sensor's zero-flow point.



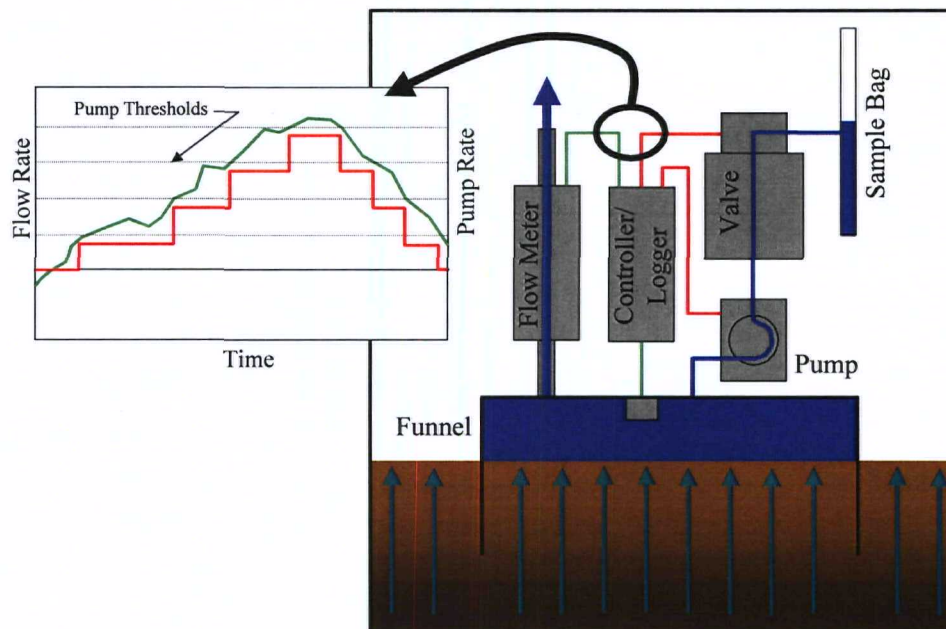


Figure 7. Functional schematic of UltraSeep system, showing the feedback system that regulates water sampling in proportion to seepage rate.

The ESM unit provides the primary data logging and control functions for the UltraSeep meter. The ESM allows programmable logging and control via analog, digital, and RS-232 signals. For the UltraSeep system, the flow sensor data are recorded as an analog signal. Typically, the control program evaluates this signal for a 5-minute averaging time and, based on the laboratory flow calibration, determines the current seepage rate. If the seepage rate is positive, the ESM activates the water-sampler pump via RS-232, and sets the pumping rate slightly lower than the current seepage rate. After a 5-minute sampling period, the flow signal is again evaluated, and the process is repeated. Approximately every 2 hours, the ESM activates the sampling valve via RS-232 and switches to a new sampling bag (Figure 7).

The water sampler consists of a high-accuracy, low-flow-rate, peristaltic pump connected in line with a selector valve. Both units are housed within a submersible pressure case. The pump (Meredos model HP60) allows sampling at user-specified flow rates ranging from about 0 to 18 ml/min. The selector valve (Valco Instruments) has six outlet ports and one inlet port. All water contact parts in the sampling system are constructed from KYNAR® or Teflon® with the exception of the PharMed® pump tubing.

In operation, the UltraSeep meter is lowered to the bottom, either directly from a boat or by divers using a lift-bag. Once the unit is settled on the bottom, divers check the seal. A period of 2 to 3 hours is generally allowed to ensure that any transient seepage response associated with the deployment activities has dissipated. The ESM unit then initiates logging and control functions. At coastal sites, a typical deployment runs over a 12- to 18-hour period to capture an entire semi-diurnal tidal cycle, although the system can be run continuously for about 4 days. During this period, the seepage rate is continuously



monitored, and up to six water samples are collected for chemical analysis. At the end of the deployment, the meter is recovered using either a lift line to the recovery boat, or by diver assistance. The meter data are then downloaded and the Teflon<sup>®</sup> sample bags recovered (Figure 8).

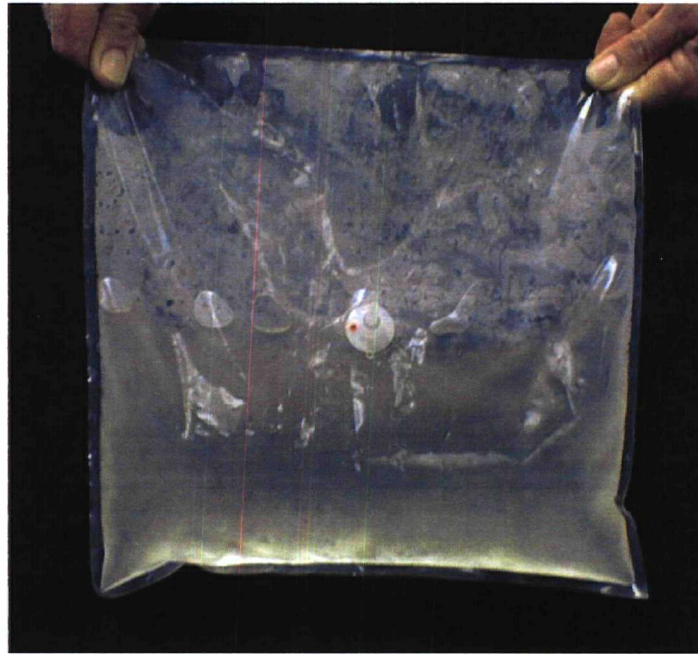


Figure 8. Teflon<sup>®</sup> sampling bag.

## TRIDENT PROBE PROTOCOLS AND PROCEDURES

### Planning Deployment

The Trident probe can be deployed in various ways, depending on the site characteristics and resources available (Figure 9). For shoreline sites where sampling occurs onshore or in shallow waters accessible by wading, the Trident probe can be directly inserted into sediments. A segmented push-pole is used to deploy the probe in waters up to 30 feet deep; the pole sections are 6 feet long and can be lengthened or shortened according to depth. Divers can directly insert the Trident probe or it can be mounted into a frame and lowered by surface craft. Each method requires different support equipment, but the following procedures cover the Trident system.

There are five major pieces of equipment required to operate the Trident system: (1) the Trident probe, (2) the communications/pneumatic cable, (3) Geoprobe®'s FC4000 field computer, (4) a laptop computer with the proper system requirements, and (5) a hand-held GPS unit with an RS-232 interface. In many cases, a 12-V deep-cycle car battery and 750-watt power inverter will be required for portable power. Appendix A provides a pre-deployment checklist to ensure all necessary items are considered.

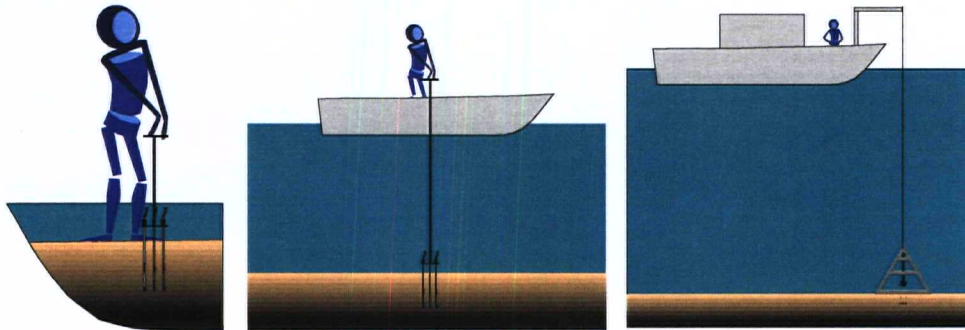


Figure 9. (Left to right) shallow-water (0 to 3 ft) T-bar, mid-range (3 to 30 ft) push-pole, and deep-water (>30 ft) deployment methods for Trident probe. Diver method not shown.

### Equipment Setup Procedures

#### Pneumatic Hammer

The Trident probe may require a built-in pneumatic hammer to insert the probe into sediments and need checking before use. It is important to oil the hammer occasionally to ensure proper lubrication of the hammer. Place several drops of pneumatic oil into the pneumatic hose connector on the input side for every 5 minutes of actual air operation (most pneumatically assisted probe insertions only require several seconds of hammer operation). Also apply a small amount of corrosion preventative behind the sliding collars on the female pneumatic hose connectors before deployment and after rinsing. Attach the regulator to a SCUBA tank and connect the hose to the input connector on the hammer housing, marked "IN". Slowly open the valve on the SCUBA tank to activate the hammer. You may want to hold a towel over the output connector on the housing, as

some oil will be ejected. The hammer will vibrate at an increasing frequency as the SCUBA tank valve is opened further, increasing air flow. You do not have to fully open the tank valve to operate the hammer. It is important to make sure the hammer has proper lubrication before storing, to prevent corrosion. You can use a hammer extraction tool (Figure 10) to remove/install the air hammer if service is necessary as described in the Maintenance section of this document.

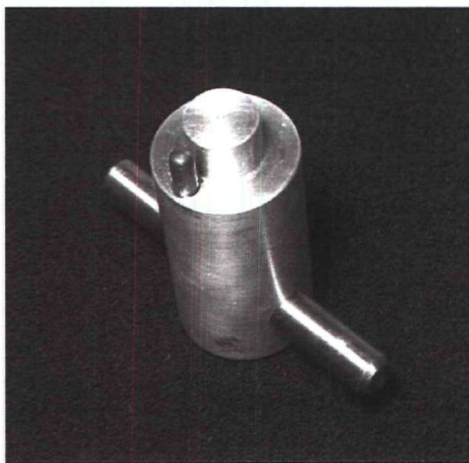


Figure 10. Air hammer extraction tool.

#### Trident Cable Assembly

The Trident cable assembly is connected to the probe at the following five points:

- Inlet port on the pneumatic hammer housing
- Outlet port on the pneumatic hammer housing
- Quick-connect for the porewater sampler
- Probe connections for temperature
- Probe connector for conductivity

It is crucial to make sure the pneumatic hose connections are properly made to prevent water from leaking into the hammer assembly and to supply/vent air correctly. A Swagelok quick-connect secures the sampling line to the porewater probe. Use the following procedure to make the pneumatic hose connections:

1. Push the male side of the connector attached to the sampling line into the female connector on the probe until it clicks (this type of connector is open only when the halves are properly coupled).
2. Attach the two cable connectors from the "Y" mold onto the temperature and conductivity probes.



3. Depending on the deployment method, zip-tie the Trident cable assembly to the short pipe extension coming from the hammer housing or onto the first section of the push-pole to prevent stress at the connections.

The surface portion of the Trident cable assembly requires connections at three points:

- Geoprobe® FC4000 field computer for the conductivity probe
- Interface cable for the temperature probe
- Quick-connect on the SCUBA regulator hose

Follow this procedure to make the surface portion connections:

1. Attach the 8-pin connector on the cable coming from the “Y” mold to the connector labeled “PROBE” at the rear of the FC4000 field computer. The f4-pin temperature cable coming from the other side of the “Y” mold is coupled to temperature interface cable having a 25-pin connector at the other end.
2. A 9-V battery connected to a mount on the adaptor cable provides power for the temperature probe. Secure battery to cable with zip-tie or tape.

#### Laptop Connections

A quad serial card is used to interface the GPS unit, the temperature probe, and the Geoprobe® FC4000 field computer with the laptop. The quad card connections are as follows:

- COM 4 to RS-232 serial splitter cable to the GPS 9-pin serial cable to GPS unit
- COM 5 to 25-to-9-pin RS-232 serial cable to temperature interface cable
- COM 6 to RS-232 serial cable to “COM 2” on back of FC4000

#### Geoprobe® Field Computer

The Geoprobe® FC4000 field computer is the standard unit Geoprobe® uses for their larger commercial conductivity probes. The unit powers the Trident conductivity probe and translates conductivity signals to numerical values for output to the GUI laptop. The conductivity probe is constantly powered by the FC4000 and data continually stream from the COM 2 serial port on the back of the unit. The real-time conductivity data are only viewed on the GUI when the “Activate Probe” button is selected, and are collected when the “Capture” button is used.

Turn on power to the FC4000; the switch is on the rear panel. The contrast dial on the front may have to be adjusted if no image is on the screen. The following menu will appear:

- Select an Option (select #1, conductivity)
- Select a Probe Option (select #1, SC400)
- Select an Option (select #2, to bypass all tests)
- Select Rod Length Used (select #2, for 2-foot rods)
- Select an Option (select #1, for wenner)

You will see a Conductivity versus Depth graph appear on the screen. When the FC4000 is used with the Trident GUI, this graph screen remains blank. To see the data plotted on the FC4000 graph, turn on the “Trigger” switch on the front of the unit and connect the “stringpot” switch to the rear of the unit. Conductivity data are plotted on the graph when the “stringpot” switch is activated. The depth data that appear are not representative of the probe depth but can serve as a reference to the data collected (due to the application of the Geoprobe® FC4000 with a custom probe).

#### Trident GUI

A MATLAB® GUI has been developed to simultaneously capture data from the Trident probes and GPS unit for real-time mapping of conductivity and temperature (Figure 11). Install this software onto a laptop with the proper requirements to run MATLAB®. “Chart View®,” which is an electronic navigation software, can be added to the laptop for navigation. If the temperature/conductivity plotting capabilities are required, you must create a digitized chart of the area. Several windows on the GUI display real-time values and graphs of temperature and conductivity along with a map display of sampled locations with their values (temperature or conductivity) represented by colored graphics (Figure 9). The Geoprobe® FC4000, the temperature probe, and the GPS unit must be powered before the “Activate Probes” button is selected on the GUI (see Appendix D for detailed GUI operations).

Individual files are created each time the “Capture” button is activated. Filenames are created using the “Station ID” entry followed by the date (automatic). All time references are based on the time set in the laptop computer. Before capturing data, it is important to allow approximately 1 minute for the temperature and conductivity probes to respond. Observe the temperature and conductivity graphs to see when the readings stabilize before capturing data.

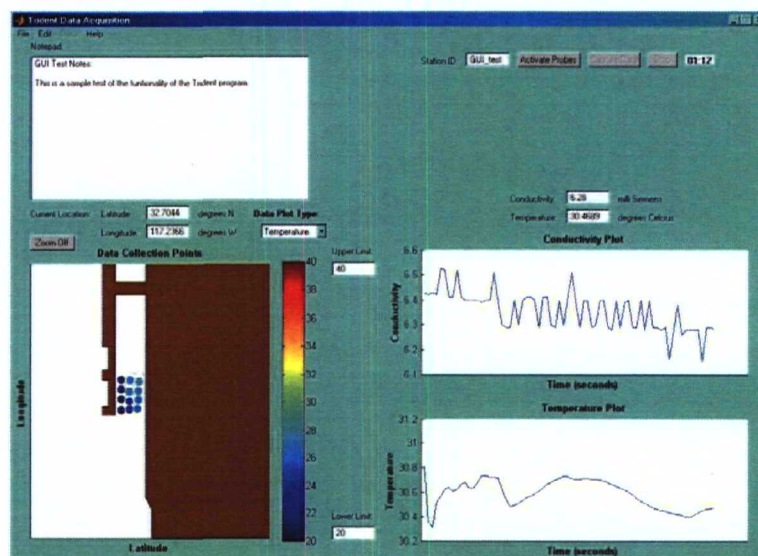


Figure 11. Trident GUI display showing map of survey area with color-assigned values at GPS-referenced sample points.



### **Deploying Trident Probe**

The Trident probe can be deployed by using a push-pole, a diver, a deployment frame, or simply by hand. The deployment method depends on the site characteristics and resources available. For above water and shallow water sites accessible by walking or wading, a sled, vehicle, or cart containing all the support equipment allows transport of the Trident system along a shoreline. The push-pole deployment method can be used from a small boat in water up to 30 feet deep and diver or frame deployment can be used in deeper water.

### **Shore Deployment**

For shore-based deployments, configure the electronics of the Trident system on a stable and portable platform. Although the hand-held GPS can move several feet from the main electronics to mark a position, an extension cable on the GPS unit allows more flexibility when moving from sample point to sample point. This flexibility can also be accomplished by using an external antenna with a longer cable. Once the Trident cable assembly has been connected to the probe and the system is ready to display data, the Trident probe can be inserted into the sediment by hand at depths up to 2 feet. A threaded push-pole can be attached to the probe for wading operations.

### **Push-Pole Deployment**

Trident probe deployments in water depths up to 30 feet deep can be performed from a small boat using the push-pole method. Six-foot sections of pole are combined to accommodate depth and can be assembled as the probe initially descends and decoupled upon retrieval or left intact. Configure the push-pole to remain attached to the probe when set in soft sediments, but configure it to detach from the probe when set in firmer sediments. In this configuration, the probe is retrieved via the cable assembly (see below).

### **Rigid Coupling**

Deploying the Trident probe while leaving the push-pole attached presents certain conditions that require attention. You must remain stationary over the site to prevent lateral forces on the probe if the push-pole is physically held while the Trident probe is operating. A 3-point anchor can hold the probe; anchors can be set past each end of the transect, another set perpendicular (astern), and lines made taut. Positions can be adjusted along the transect by slacking one anchor line and pulling in on the other. In many cases, once the Trident probe has been set into the sediment, the push-pole will remain vertical after release, as long as the height of the push-pole above the water surface is kept to a minimum. If this is the case, the boat position should be maintained close to the push-pole without the possibility of drifting into the pole or pulling the Trident probe out of the sediment via the cable assembly.

### **Detachable Coupling**

To decouple the push-pole from the Trident probe, the short section of pipe with two short rods protruding from each side is threaded onto the top of the air hammer housing. The initial push-pole that attaches to the Trident probe for this purpose has slots that engage these rods with a counterclockwise push-and-twist motion (Figure 12). A spring, tethered to the pole connector, is placed between the two connectors before being coupled. This spring keeps the probe attached until probe placement is completed. A

clockwise twist on the push-pole disengages the probe. The pole can then be pulled from the water while the Trident probe remains in place. This bridle relieves stress on the probe connections when the cable assembly is used to pull the probe back to the surface. A stress relief bridle on the hammer housing is fastened to the cable assembly, which leaves slack on the probe connections when taunt.



Figure 12. Detachable push-pole coupling.

#### **Setting Trident into Sediment**

Lower the Trident probe with the push-pole while maintaining minimal slack in the cable assembly until it contacts the sediment and continue to push the probe until it is set. In firmer sediments, you must use the air hammer to assist the insertion. Turn on the SCUBA tank valve while pushing on the pole until the Trident probe can no longer be inserted further. You can bend the probes if objects are buried in the sediment. Hard objects such as rocks can be felt via the push-pole. Reposition the Trident probe if there is any question of striking hard objects. If the Trident probes get bent, they can be easily straightened by hand.

#### **Diver Deployment**

The Diver method for deploying the Trident probe offers rapid repositioning between sample locations but requires communication between topside and the divers. An underwater communications unit allows verbal communications between divers and Trident GUI operators, but simple signals can be worked out if an underwater communications unit is not used. A partially submerged metal pipe struck by a hammer can produce audible signals for communications to the divers. A buoy with a line held by a diver can be bobbed on the surface for return visual communications. Communications would be necessary for repositioning the Trident probe, actuating the air hammer, and for confirming placement. A measuring tape or marked line marks a transect along the bottom and guides the divers positioning the probe. The Trident probe is set up with a short section of pipe threaded into the hammer housing so it can be used as a handle.



### Frame Deployment

The Trident probe can be mounted into a frame for deployment from a support vessel's davit. Although this method was never used during development, the concept is straightforward. A 4-foot pipe, threaded into the top of the Trident air hammer housing, passes through a plastic guide at the top of a 3-foot high deployment frame. A locking pin, placed through a hole in the pipe above the guide secures the Trident probe within the frame when out of the water. A shackle attached to the top of the pipe connects the davit cable. Once the Trident probe and frame are suspended for deployment, the locking pin is removed. The Trident is lowered to the bottom and the air hammer is actuated for insertion.

### Porewater Sampling

The Trident probe allows the collection of porewater at the same depth the conductivity and temperature are measured, up to 2 feet into sediment. Attach the priming syringe to the closed luer-lock valve on the 1/8-inch Teflon<sup>®</sup> tubing coming out of the cable assembly, pull vacuum on the syringe, and lock the plunger using the locking rod (Figure 13). Open the luer-lock valve and allow the priming syringe to collect 50 ml of water to prime for sample. If 50 ml of water is not collected, close the luer-lock valve, disconnect the syringe, empty, and repeat vacuum until a total of 50 ml has passed through the sampler. Repeat this process with the sample syringe, evacuating air from syringe only if necessary, until sample size is acquired. Larger porewater collections can be made using a sample bottle plumbed between the Trident sampler and a vacuum pump. Note that some sediments are not conducive to direct porewater sampling due to fine grain size. It may help to push a few milliliters of water through the sampler, using the priming syringe as the probe moves down through the sediment.

Clean the porewater sampler before each sample collection. Place the tip of the porewater sampler into a collection container and push 100 ml of warm Alconox<sup>®</sup> solution (2%) through the sampler with a specified syringe. Follow this cleaning with 100 ml of deionized (DI) water, using a syringe dedicated for this purpose.

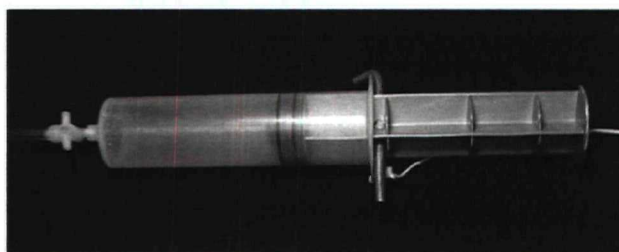


Figure 13. Syringe with locking rod through plunger.

### Maintenance

Thoroughly rinse off the Trident probe and cable assembly while all probe connections are still in place. Pay particular attention to the pneumatic fittings. Put the porewater probe tip in a container of freshwater and, using the priming syringe, draw at least 100 ml of freshwater through the porewater sampler to rinse and remove any particulates. Remove the probe tip from the container and draw remaining water from the sampler and line. If the sampling line was exposed to any free product, you should flush line with



warm Alconox® before rinsing. Disconnect cable assembly and place a few drops of oil into the air intake port of the pneumatic hammer. Apply an anti-corrosive to the pneumatic quick-connects.

The pneumatic hammer should provide long service when properly lubricated and protected from water entry. If you must access the hammer, remove the top cover plate on the housing and use the air hammer tool to unscrew the hammer assembly. The hammer assembly has only three parts: the cylinder, the piston, and the valve body. Lift the valve body off the hammer cylinder to access the piston. Clean and lubricate the piston and cylinder with light oil. Apply grease to the threads on the cylinder, replace the valve body, and use the air hammer tool to screw the hammer assembly into the housing.

## ULTRASEEP PROTOCOLS AND PROCEDURES

### Planning Deployment

Planning the deployment period of the UltraSeep is important, as maximum seepages occur during periods of extreme tidal cycles. If a single tidal period of approximately 12 hours is sampled, Start the sampling sequence at the beginning of the high tide. If sampling occurs over several days, you might want to start the sampling sequence just before a high or low tide.

Before heading out to the field, make sure you have all necessary items for the deployment. Appendix C covers all the items required for using the UltraSeep. Set up programs for the UltraSeep before fieldwork so that pre-deployment programming goes quickly. Clean UltraSeep surfaces that come in contact with sample waters (sample tubing and interior of funnel) and attach sample bags before deployment.

### Battery Charging

The UltraSeep uses the latest in battery technology to power the meter up to 4 days while providing exceptional safety during transport and handling. A 12-V, 105-Ah, deep-cycle, aggregate glass matt, sealed battery supplies power. While this type of battery technology minimizes off-gassing, **vent the battery housing while charging** to prevent explosion (also remove the threaded plug at the top of the housing during storage). Before charging, remove the threaded plug from the top of the battery housing and insert tubing at least 10 inches into the housing (Figure 14). This tubing can be connected to a low-flow air source or an aquarium air pump, which provides a positive airflow during the charging phase.



Figure 14. Top of the battery housing showing power connector and vent hole (without plug).

To maintain optimum battery performance, the battery should be fully charged before storage and recharged once every 4 months. The charging unit, a CT Chargetek 500, is fully automatic and can be left on charge indefinitely, without damaging the battery. First, connect the charger to the battery via the 2-pin connector on the top of the housing. These connector pins are “hot,” so prepare the area so that nothing will inadvertently short the pins, which could cause permanent battery damage and a possible explosion. Once the charger is connected to the battery, plug the unit into a standard 115-V outlet. It is highly unlikely, but if the “service” light on the charger illuminates, unplug the charger and test for possible causes. The red “fast” charge light will remain on until the battery has received sufficient charge and the light illuminates green, indicating a “float” charging phase. It is preferable to leave the battery charging on “float” for several hours, but is not necessary. Unplug the charger from the AC outlet before disconnecting the charger from the battery. Inspect the threaded plug at the top of the battery housing and wrap it with Teflon<sup>®</sup> tape before re-installing.

#### **Preparations for Cleaning**

The solutions used for cleaning the UltraSeep will differ according to the type of analysis performed. A warm 2% Alconox<sup>®</sup> solution is used in the cleaning process in preparation for sampling organic compounds (most common use) and a warm 2% Rutherford Backscattering Spectroscopy (RBS) solution for sampling metals. Nitric acid is used if metals are going to be measured and must be diluted to a concentration of 10%. The last fluid used in the process will be 18 mega-ohms of DI water. Teflon<sup>®</sup> sample bags are attached to the DI primed sample lines once the cleaning process is complete. See Appendix E for detailed cleaning instructions.

Make sure the pump tubing inside the valve housing has been loaded into the pump head. Try not to disturb the knurled screw on the pump head; this screw controls the pressure of the rollers on the tubing and affects flow. The adjustment screw should be set to the manufacturer’s specifications, but a 1¼ turn open from the full stopped position should be close.



## Software

Two programs are needed for programming the ESM-1 controller/logger and one for the MiniLogger. A text editor is needed to write/change the programming scripts for the ESM-1; the developers of UltraSeep use ConText Editor. The other is Hyperlink, which communicates with the ESM-1. Programs to run the ESM-1 for actual sampling are the “main” and “pump” files. Other programs are provided for decontaminating the meter, and for valve and pump testing. A program named “Flowm” is used to program/communicate with the MiniLogger. Create desktop shortcuts to find these programs easily.

## Preparing to Communicate with Meter

Two components on the meter require computer programming before deployment. One is the ESM-1, a data logger/controller for the valve and pump, and the other is the MiniLogger for the ultrasonic flow meter. To communicate with the meter, the power cable on the meter must be connected to the battery. To connect a computer to the ESM-1, plug the wet-pluggable mini-connector cable from the small interface box into the ESM-1 (serial port 1) and the RS-232 (DB-9) connector from the interface box into the computer (Figure 15). The computer connection for the MiniLogger is made via the 100-foot MiniLogger communications/solenoid cable that has a “T” mold going to two shorter cables. One of these short cables, labeled “com mini”, is then connected to the “mini logger com” cable having the DB-9 computer connector. Plug the female 3-pin connector on the 100-foot cable into the male 3-pin connector on the MiniLogger and the DB-9 into the computer. A cover for the display panel on the MiniLogger must be left in place when outside, as sunlight affects the display and makes it unreadable until the panel cools.

The ultrasonic flow meter requires “zeroing” once the UltraSeep is submerged; this procedure ensures accurate flow measurements and should be conducted for each deployment. A 24-VDC source is needed to supply power to the solenoid valve, plumbed in-line with the flow sensor. To activate the valve, two, small, 12-V gel cell batteries connected for 24-V output can be used. While the solenoid valve is powered (closed), the water inside the flow tube is not moving and the flow meter can be zeroed. An adaptor cable has two leads for battery connections and is connected to the short cable coming from the “T” mold, labeled “solenoid 24V”.

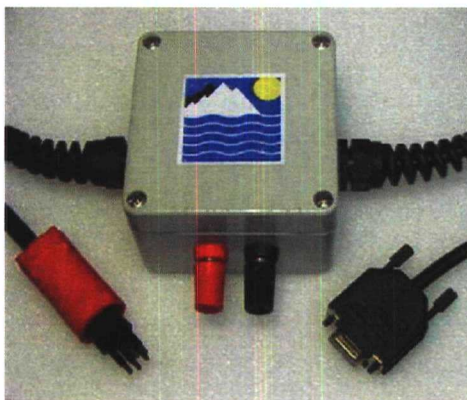


Figure 15. ESM-1 computer interface.

### **Programming UltraSeep**

Program the MiniLogger before the ESM-1. Check the display panel on the top of the MiniLogger to make sure it is getting power; characters will be visible. Select the "Shortcut to Flowm" from your computer's desktop. Zeroing the flow sensor should be done after the MiniLogger and ESM-1 are programmed and the UltraSeep is in the water. See Appendix H for "zeroing" and programming procedures for the MiniLogger.

Once the MiniLogger has been programmed, connect the ESM-1 interface box from the computer to serial port 1 of the ESM-1. If remote monitoring of the ESM-1 is desired, connect the 100-foot com cable between the interface unit and the ESM-1. Two files are uploaded to the ESM-1 for programming; these files are the "main" and "pump" files. The "main" file is edited and used to program the delay and sampling times, while the "pump" file is edited and used to control the pump. Details for programming the ESM-1 are in Appendix G. Log the ESM-1 start time as well as the start time for the sampling sequence to determine sample periods for each sample bag and when the sampling sequence will finish.

### **UltraSeep Deployment**

Review the pre-deployment checklist in Appendix D and ensure that the valve stems to the sample bags are in the open position. Remove wheels from the UltraSeep frame once the unit is suspended. Traditionally, divers have been used during deployment of the UltraSeep to facilitate priming the ultrasonic flow tube and ensuring a good placement into the sediment. Typically, the UltraSeep has been deployed into the water using a winch and release shackle attached to the meter's lift bridle. If the sediment site looks good for deployment directly under the UltraSeep, then it can be lowered to the bottom as long as the support boat is operating in calm waters. Lift bags are usually used and allow divers to maneuver the meter to a suitable location (Figure 16). It is important that the divers do not allow air bubbles to enter the funnel.

### **Zero Flow Meter**

The ultrasonic flow sensor should be "zeroed" to provide accurate flow data. It is very important to prime the ultrasonic flow tube using the primer bulb to remove any air bubbles in the tube or under the funnel before zeroing. The funnel should be cleared first, followed by the flow tube using the suction side of the priming bulb. A 24-V source is attached to the MiniLogger cable to close the in-line solenoid valve during the zeroing process.

The zeroing procedure can be performed after the UltraSeep has been set into the sediment. Use this method of zeroing if bottom-water temperatures are significantly different than temperatures at the surface. This method of zeroing requires the MiniLogger cable to remain attached to the meter. Once completed, cable ends are dummy-plugged before tossing the cable into the water. Use other zeroing options if it is preferable to deploy the UltraSeep without leaving cables attached. The unit can be suspended near the bottom while the flow sensor is zeroed, or it can be zeroed just under the surface if temperature and salinity are similar to benthic waters. Once zeroed, the UltraSeep can be brought onboard and the cables removed and dummy plugs put on



connectors. Priming the flow tube and removing bubbles from the funnel will have to be performed again.



Figure 16. Diver using lift bag to deploy UltraSeep.

#### Setting UltraSeep

Gently lower the meter into the sediment to avoid disruption. The flange should be set level with the sediment surface. If sediments are extremely soft, it may help to have the lift bags or dive vests slightly more buoyant for a controlled push into the sediment. If force is required to insert the UltraSeep, use vertical pushing or “bouncing” on the meter frame. Use a slight back-and-forth rocking motion on the frame as a last resort. Relocate the UltraSeep if an object under the sediment surface interferes with placement. The idea is to place the meter into the bottom while minimizing disturbance of the sediment (Figure 17).

The UltraSeep can be marked with a buoy, provided there is enough slack in the line to account for high tides over the course of the experiment and there is no threat of boat traffic or people to disturb the marker buoy. This marking also allows for recovery without the need for divers. The unit can also be tethered to a structure, such as a nearby piling, if marker floats are risky and recovery without divers is planned. In many situations, a marker float or tethered line attached to the meter is undesirable, but the meter can be relocated using a GPS unit or marker buoy anchored adjacent to the meter. If lines are attached, the possibility of the UltraSeep being disturbed must be considered a possibility and could affect measurements and samples.

The meter may also be deployed from shore if the waters are too shallow for a boat deployment. In this case, it may be useful to place the meter placed onto a makeshift sled to transport it to a location deep enough for the UltraSeep to operate (25 inches deep at lowest tide). Another option is to remove the battery from the frame to lighten the UltraSeep and power the meter from shore via the 100-foot power cable. The battery, if left on the frame, helps stabilize the meter and minimize any physical disturbances from passing waves and wakes. If the remote power method is used, consider water conditions.

An ambient water sample collected near the sediment surface, close to the UltraSeep location, is also recommended for a “baseline” chemical reference. Divers can make the water sample collection immediately before insertion of the meter or after suspended sediments have cleared.

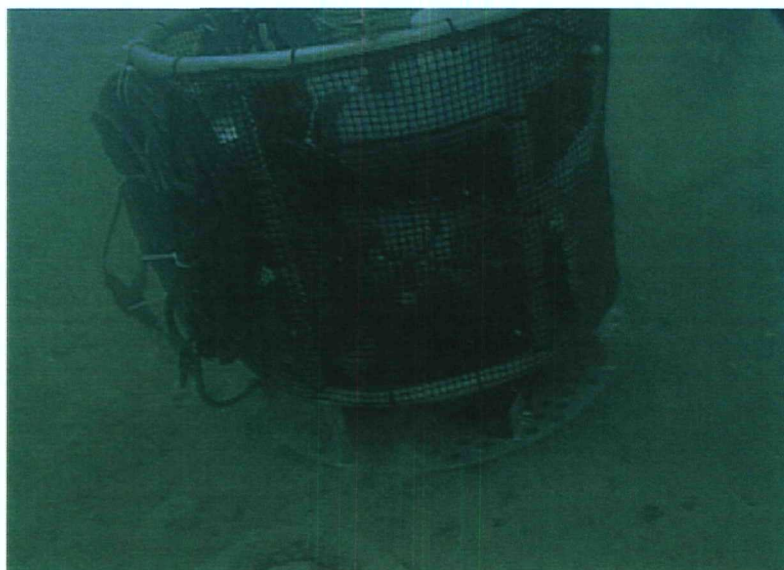


Figure 17. Seepage meter set into sediment up to flange.

## **Data Collection and Analysis**

### **Downloading Data**

Connect computer(s) to the ESM-1 and the MiniLogger as previously described in “Preparing to Communicate with Meter.” Procedures for downloading data from the meters are in Appendix H. Check to confirm that the position of the selector valve cycled properly. Use the “openpipe” function after downloading data to make sure that data are on port #6 (see Appendix H).

### **Plotting Data**

Microsoft® Excel is used to process the ESM-1 and MiniLogger data. A template file, “Seep meter Excel Template.xls,” processes the ESM-1 data. A template for the MiniLogger “Minilogger Excel Template.x,” processes the raw ultrasonic flow data.

ESM-1 data processing instructions are on the "raw data" sheet of the "Seep meter Excel Template" and the "processed" sheet of the MiniLogger template. Data processing instructions are in Appendix I for the ESM-1 and Appendix J for the MiniLogger.

### **Maintenance**

Thoroughly rinse the UltraSeep with freshwater after retrieval, including the interior of the funnel. It is important to flush the inside of the ultrasonic flow tube; Use a garden hose placed over the outlet tube on the top of the housing, flush the inside. Rinse the sample tubing with DI or freshwater by extending the disconnected inlet sample line going to the funnel. Place the extended line-end into freshwater and run the "1minPump.esm" program or the "Clean4.esm" program for a longer flush.

Fully charge the battery after each use and, periodically, to maintain battery strength; refer to the "Charging Battery" section.

It is highly recommended that you unload the PharMed tubing from the peristaltic pump head to prevent permanent deformation and weakening during long storage. Inspect this section of tubing before deploying the UltraSeep, especially if it has been stored in a loaded state or if it is getting old. Check housing O-rings periodically; clean and silicon grease them, if necessary.

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## APPENDIX A: Trident Checklist

<b>Water Sampling</b>					
• Adaptor tubing (Tygon)					
• Syringes (vacuum pump?)					
• Vials & label					
• Refractometer					
• Alconox® and DI water					
• Haz Waste Container					
<b>Temperature Measurement</b>					
• Serial Adaptor Cables					
• Battery (9V)					
<b>Conductivity Measurement</b>					
• Field computer – FC4000					
• RS-232 adapter cables					
• Floppy disk					
• Stringpot cable					
<b>GPS 48</b>					
• Site GPS coordinates					
• Spare battery (AA) (4)					
• RS-232 extension cable					
<b>Trident</b>					
• Cable Assembly					
• Push-pole sections					
• SCUBA tank(s) and reg					
• Pneumatic oil					
• Trident kit box					
<b>Boat Stabilization</b>					
• Anchors (3)					
• Lines (3)					
<b>Laptop</b>					
• Power cord					
• Quad serial card					
• RS-232 adapter cables					
• MATLAB® program					
• Local e-chart Chart View					
<b>Other/Misc.</b>					
• 12-V car battery					
• 750-W power inverter					
• Teflon® tape and zip ties					
• Cart & secure lines					
• Tarp					
• Logbook					

## APPENDIX B: Trident Software Operational Instructions

### Introduction

This document contains and describes the operational instructions for using the Trident Probe Software. It is not meant to be a reference source for the corresponding MATLAB® source code.

### Setup And Installation

To run the Trident Probe software, at least a basic version of MATLAB® must be installed. The Trident Probe software does not use any special MATLAB® toolboxes, however the software was written using MATLAB® version 6.0.0.88 (R12) and should probably be run on similar versions as internal functions and functionality changes that occurred with subsequent releases might cause parts of the software to not function correctly.

### MATLAB Installation

For specific instructions on installing MATLAB®, please see the MATLAB® documentation.

### The Trident Probe Software Installation

The Trident Probe software (the MATLAB® m-files and such) is currently located in the C:\trident directory on the **trident-one** computer. The only subdirectory actively used by the software is the data\_files directory. After a data capture is performed, the data are written to flat files in this directory that must exist before running the data capture portion of the Trident Probe software.

In addition, the Trident Probe software help files are located within MATLAB®'s directory structure so that they can be read from within MATLAB®. On **trident-one**, these files are located in the C:\matlabR12\help\trident directory.

Some third-party files existing within the Trident Probe software directory are also needed: the .bln files are the map files. Currently only sdbay.bln exists, but contains the latitude/longitude coordinates for San Diego Bay. The uigetfiles.\* files can be used to display an open files dialog and allow the user to select more than one file. This file will be useful in creating an application to read the raw data files generated by the Trident GUI.

### Running The Trident Probe Software

#### *Launching the Program*

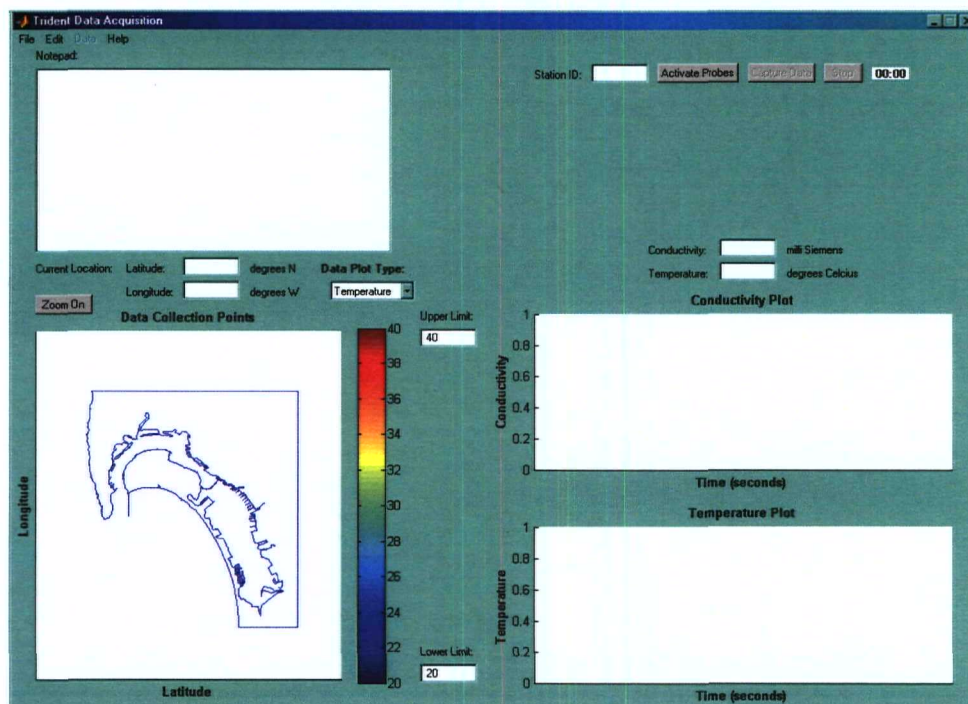
To run the Trident Probe software, first launch MATLAB®. Then, if the file, trident.m, is not located in MATLAB®'s search path, you will have to add it to the search path to keep from manually having to change into the C:\trident directory every time you start MATLAB®.

To add it to MATLAB®'s search path, follow these steps:

1. From the main MATLAB® window, click **File >> Set Path**.
2. Click the **Add Folder** button.
3. Using the navigation window that pops up, navigate to the directory you wish to add to MATLAB®'s search path. In our case, probably C:\trident.
4. Click **OK** to accept the selected path.
5. The previously selected path will now appear at the top of MATLAB® search path list.
6. Click **Save** to save the changes.
7. Click **Close** to exit the Set Path window. **Note: all changes take effect immediately.**

At this point, if the path was set up correctly and all the files are located in the specified directory, the Trident Probe software should be executable by typing the word 'trident' at MATLAB®'s >> prompt.

The Trident Probe GUI should now be displayed as shown below:



### Configuring the Trident Probe Software Preferences

The user should probably configure any preferences he/she would like before running the data collection portion of the program. Click **Edit >> Preferences** from the menu bar.

The preferences menu displays as shown in the figure below.

If the Trident Probe software is being run for the first time, the default settings display. After changes have been made and saved, a file called preferences.mat is created and loaded on subsequent launchings of the Trident Probe software. If this file is ever deleted, the default settings are once again used.

If COM port changes are made, as noted above, they are immediate. For this reason, the availability of the preferences menu is disabled during data acquisition.

The user can select the default map that displays upon the starting of the application. This display is useful if the application is being heavily used in a certain region and keeps the user from having to continuously manually change the location map. A small picture of the map should display in the window to let the user see what the selected map looks like.

Two checkboxes are to the right of the map display. The first checkbox defines whether the application should prompt the user before exiting. The second checkbox defines whether or not the application confirms file deletions.

The default color bar settings allow the user to choose the number of colors used by the color bar. The higher the number of colors means a smoother transition (i.e., “fading” from solid red to solid orange) between data values, but also means that “close” data values will have very similar colors. The lower the number of colors means a very choppy and abrupt (i.e., jumping from solid red to solid orange) transition

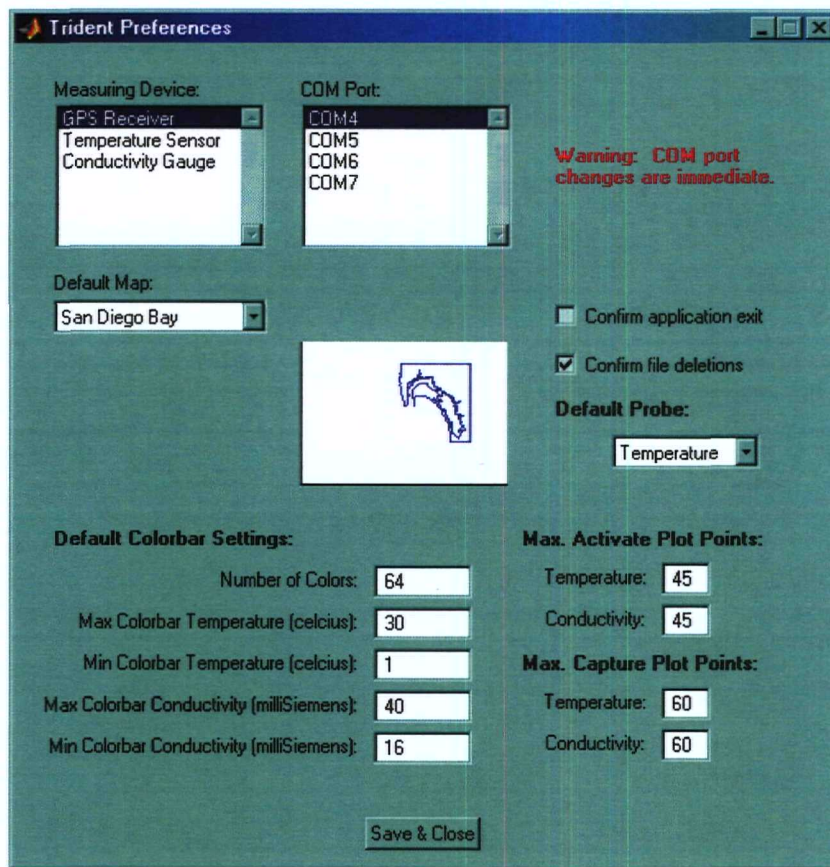


between data values and means that even close data values may appear completely different or have identical colors, depending on where the color index lies in comparison to the data set.

It also allows the user to specify the minimum and maximum default temperature settings for the temperature and conductivity plots. These values can also be set via the main Trident Probe software window. These values, if changed, are saved to the preferences file.

By changing the Default Probe setting, users can specify what data they want to plot. They can also change what they want to plot via the main Trident Probe software window, but unlike the min/max temperature/conductivity values, this change is not saved to the preferences file.

Finally, the user can specify the maximum number of data points allowed in the temperature and conductivity plot windows. Two sections exist, one for when the probes are active, and the other for when a data capture is performed.



### Capturing Data with the Trident Probe Software

Before data capturing can be performed, the three necessary serial devices, the GPS receiver, the Temperature probe, and the Conductivity probe should all be powered on and ready for use. In the case of the GPS receiver, one must ensure that the device has acquired the needed satellite signals and is ready for use. The necessary cabling must be connected to the Trident probe. **Thorough and detailed instructions on how to connect and power these devices begin on page 11 of this document.**

To begin the data capture, the probes must first be activated. To do this, click the **Activate Probes** button. **Note that data capture refers to the actual portion of running the software where the software is writing the data to the flat files (and when finished will display the color shaded plot accordingly).**



**Probe activation, merely means the probes are turned on and the data transmitted via the serial cables is being received and plotted by the software.** While the probe activation should be done after the Trident Probe has been deployed and is firmly in the sediment, it is not required. If this is not the case, the GPS reading taken at the onset of the probe activation may differ from the actual GPS reading taken at the onset of the data capture.

With the probes activated, the Temperature and Conductivity plots will begin plotting the data transmitted from the probes. The Conductivity reading should stabilize rather quickly, while the Temperature plot might need a minute to stabilize. Temperature stability is essential for capturing correct and valid data because during the data capture phase the data from the probes are written out to the flat files at 1 Hz. The same data is saved internally to MATLAB® and used to calculate and create the color-shaded dots in the Data Collection Points window, which are averaged over the entire span of the data capture, i.e., the temperature curve should decay exponentially before stabilizing. If the data capture is performed while the probe readings stabilize, the average value computed by MATLAB® will be higher than the real-world value because the higher values on the decaying portion of the exponential curve have been used to calculate the average. Once the temperature readings have stabilized, i.e., the graph is essentially horizontal, a successful (meaning the data collected will be true and valid) data capture can be performed.

Currently, the MATLAB® code for the Temperature and Conductivity data plots is hard-coded to hold 30 data points before scrolling off the plot.

To begin the data capture, make sure a Station ID has been specified and click the **Capture Data** button. The current location/date/time will be received from the GPS receiver and stored. The location values display in the relevant fields in the GUI. The data plots clear and the internal Temperature and Conductivity buffers reset to zero. At this point, the software collects and plots the transmitted data at 1 Hz. The data is plotted to the Temperature and Conductivity plot windows and also written out to the flat files. The timer in the upper left corner display how long the data capture process has been running and when sufficient data have been collected for this point (usually no more than a minute); click the **Stop** button to end the data acquisition process. At this point, the flat files will be closed for writing and the average temperature and conductivities will be calculated. Depending on what plot type is specified for the Data Collection Points window, a color-shaded dot representing either the Temperature or Conductivity will appear at the location specified by the GPS reading. For this reason, a map of the harbor or coastline where the Trident has been deployed is useful for telling the user where exactly the data point is located. The flat files are stored in a subdirectory from the Trident files called **data\_files**. The filename format is the Station ID followed by a date/time stamp. The extension placed on the file is .raw, for raw data.

This process can be repeated for as many locations the user needs to evaluate. Currently, the map image with the color-shaded points cannot be exported to a picture file, except as a "Print Screen" option.

### **Other Trident Software Options**

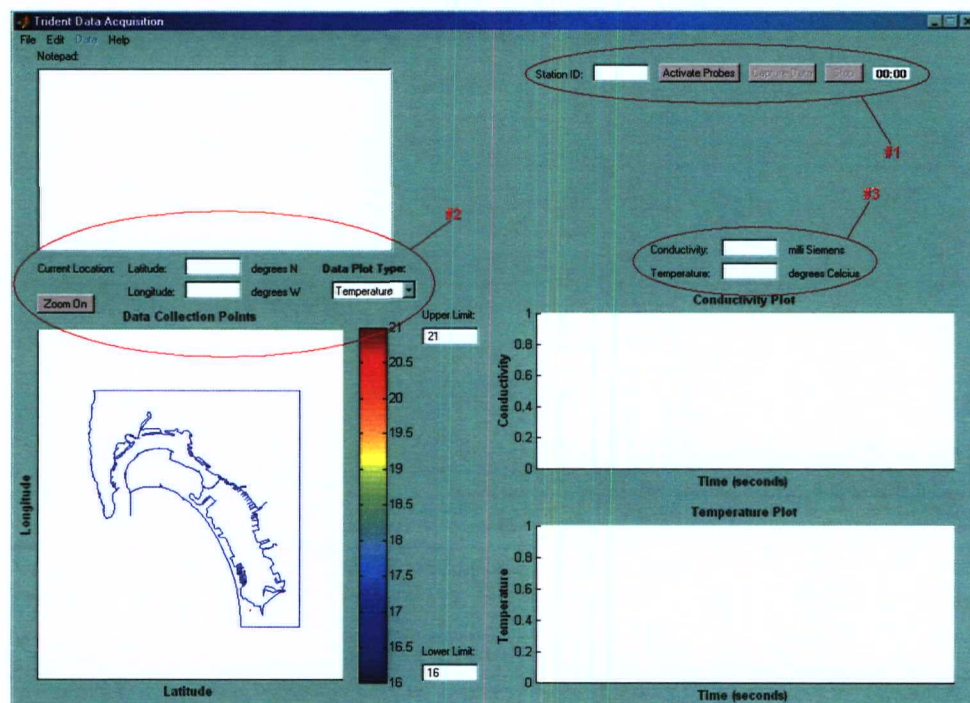
The Data Collection Points window has a zoom feature that, when enabled, allows the user to zoom in on specific areas. This feature is extremely useful if a coastline or harbor map is being used as the user can then zoom-in on the data points collected and see exactly where they lie in relation to other harbor/coastline landmarks.

This map window also has a plot-type feature that allows the user to switch back and forth between temperature and conductivity plots. Simply changing the plot type from the drop-down list will update the map with the correct data. The color bar has a text field for setting the lower and upper limits of the color bar. For these setting to take effect, the user must change the limits to the values needed and then select the plot type from the plot type drop-down list. This change causes the software to recapture the entered limits and adjust the color bar and data map accordingly.

The Notepad section is useful for noting specific information about a certain data run, or data collection point. It is not required to be used; however, if it is, the data contained there will be written to a flat file when the program is closed.

### Trident GUI Layout

The layout for the GUI is shown below:



## Section 1 - The Control Buttons

**Station ID Field:** The Station ID field allows for a unique identifier to be associated with the acquisitioned data. The name in this field is used as the first part of the filename of the acquisitioned data. Please use “ ” (underscores) instead of spaces. The full filename consists of the string from this field and a date/time stamp. The default extension for these data files is ".raw". Since this field is required, data capturing cannot occur until this field is populated; however, since the date/time stamp for each file is unique, no error checking is done to ensure that this field is changed between point acquisitions.

**Activate Probes:** The Activate Fields button is a toggle button, and thus has two states, on and off. Upon the first pressing of this button, the COM ports are assigned to each of the measuring devices: the GPS receiver, the Temperature probe, and the Conductivity probe. Subsequent activations do not reassign the COM ports. The GPS receiver is queried once and the Latitude/Longitude fields (as described in Section 2 below) are updated to reflect the current position. The Temperature and Conductivity probes are then queried at a frequency of 1 Hz for as long as this button is activated. The data read from the probes are plotted continuously and in real time in their respective axes in the lower right corner of the GUI. The Temperature and Conductivity fields (as described in Section 3 below) are updated to reflect the current probe readings. This button can be deactivated in two different ways: by clicking the button to the off position, or by clicking the Capture Data button.

**Capture Data:** This button is only enabled when the probes are active, i.e., when the “Activate Probes” button is on. As soon as the data capture begins, the button is again disabled, the temperature/conductivity plots and the counter timer are reset to empty plots and 00:00, respectively. The functionality of this button is identical to the Activate Probes button, except for the COM port assignments. In addition, the data from the probes are written to a .raw data file for later analysis. The timer to the right of the Stop button displays the length of time the data have been captured. Data are captured until the Stop button is pressed.

**Stop:** The Stop button is only enabled after the Capture Data button has been pressed and is immediately disabled after being pressed. After this button has been pressed, the mean temperature and conductivity are calculated for the current data set, and depending upon what data plot type is specified (as described in Section 2 below), the mean is plotted as a point on the map with colored shading that dictates the value at that point.

## Section 2 - Data and Map Functions/Features

**Zoom:** This button toggles the zoom feature on or off. When on, the user may either click on the map to zoom in on a specific point, or may click and drag the mouse to select an area on which to zoom. Right-clicking the mouse will zoom out. Clicking the zoom button again will turn the zoom feature off and freeze the map at the current level.

**Current Location:** The current latitude/longitude displays in decimal degrees. This field is only updated once per probe activation or data capturing, so the GPS receiver does not need to be held in place above the deployed Trident probe once the position is captured. Once the temperature and conductivity plots show data plotted, the GPS receiver may be moved.

**Data Plot Type:** This drop-down list gives the option for what data is to be plotted in the data map. If Temperature is selected, any collected temperature data are plotted and after capturing data is complete, the newly collected temperature data are also plotted. The converse is true when Conductivity is selected. Because the map is updated after a capture cycle is complete, this feature is temporarily disabled during data capturing.

**Map:** The data plot consists of color-shaded points that represent either the temperature or conductivity at specific coordinates on the map. The data displayed are determined by the selection in the data plot type field.



**Color Scale and Limits:** The lower limit field specifies the lower limit of the color band and the upper limit specifies the upper limit of the color band. The color band is not updated until either a data capture is performed or an option in the data plot type is selected or re-selected.

### Section 3 - Temperature and Conductivity Data/Plots

**Probe Data:** As the probes are queried, whether in activation mode or data-capturing mode, these fields display the last value read from the probes.

**Plots:** As the probes are queried in activation or data capturing mode, these plots track the changes. The time axis always starts and stays at zero, so the points are "packed" in from the right. These plots are reset (erased) each time the probes are activated or a data capture is performed.

### Trident Supplemental Information

The temperature probe returns the temperature in degrees Celsius.

The conductivity probe returns the conductivity in milliSiemens.

The porewater probe allows for the extraction of water (for sampling) while the probe is deployed.

The air hammer acts like a jackhammer in that it assists the probe to be inserted further into the sediment.

### GPS Receiver

The GPS receiver uses the following:

- Port COM4 – Currently has a splitter to share the GPS data w/ another COM port (e.g. COM7) that would be read by another mapping software program (e.g., ChartView™).
- The black, 9-pin serial cable with the red velcro strap.
- The 9-pin serial splitter was created for use with the receiver so that the to National Marine Electronics Association (NMEA) output can be used simultaneously in MATLAB® for the Trident program and ChartView™, which currently contains the full map of survey area. (optional).
- Four AA batteries.

The GPS receiver generates the following serial output according to NMEA standards. The only lines used by the Trident GUI are marked in red as follows:

\$GPRMC, POS.UTC, POS\_STAT, LAT, LAT\_REF, LON, LON\_REF, SPD, HDG, DATE, MAG\_VAR, MAG\_REF\*CC<CR><LF>

POS.UTC - UTC of position. Hours, minutes and seconds [fraction (opt.)].

(hhmmss[.fff])

POS\_STAT - Position status. (A = Data valid, V = Data invalid)

**LAT** - Latitude (llll.ll) (ddmm.mm - whole degrees and decimal minutes)

**LAT\_REF** - Latitude direction. (N = North, S = South)

**LON** - Longitude (yyyy.yy) (dddmm.mm - whole degrees and decimal minutes)

**LON\_REF** - Longitude direction (E = East, W = West)

SPD - Speed over ground. (knots) (x.x)

HDG - Heading/track made good (degrees True) (x.x)

DATE - Date (ddmmyy).

MAG\_VAR - Magnetic variation (degrees) (x.x)

MAG\_REF - Magnetic variation (E = East, W = West)  
 FIX\_MODE - Position Fix Mode ( 0 = Invalid, >0 = Valid)  
 SAT\_USED - Number Satellites used in solution  
 HDOP - Horizontal Dilution of Precision  
 ALT - Antenna Altitude  
 ALT\_UNIT - Altitude Units (Meters/Feet)  
 GEO - Geoid/Elipsoid separation  
 G\_UNIT - Geoid units (M/F)  
 D\_AGE - Age of last DGPS Fix  
 D\_REF - Reference ID of DGPS station  
 CC - Checksum (optional)  
 <CR><LF> - Sentence terminator (carriage return and line feed)

The tags used by the Trident GUI are in bold above. For accurate data plotting, any coordinates in the southern or western hemispheres are stored as negative numbers; however, are displayed as positive numbers since the GUI specifies the direction.

### **Temperature Probe**

The Temperature probe uses the following:

- Port COM5
- A heavy black cable with a round, 4-pin connector (the four pins form a square) on one end connected to a 25-pin to 9-pin gray serial cable on the other end. A 9-V battery to power the SBE temperature probe is connected via a red/black twisted-pair of wires attached to the gray 25-pin to 9-pin converter.
- The serial output from the temperature probe is in decimal degrees Celsius (format: cc.cccc).

### **Conductivity Probe**

The Conductivity probe uses the following:

- Port COM6
- A gray serial cable with 9-pin connectors on each end.
- The GeoProbe® FC4000 field computer.
- Power supplied by the field computer (110v).

To get the FC4000 field computer into the correct mode to transmit data via the serial port, turn the unit on and select the following menu options:

- 1 - Conductivity
- 1 - For SC400
- 2 - To bypass all tests (if this is indeed the user's wish)
- 1 - For 1m rods
- 1 - For Wenner type conductivity probe

The serial output from the conductivity probe is in decimal milliSiemens; however, since the decimal is not transmitted with the data, the number is divided by 100 to get the actual decimal. (serial format: cccccc, program format: cccc.cc)

## Appendix C: Checklist For UltraSeep

<b>Prep and Sampling</b>				
• Log Book				
• Manuals (ESM-1, MiniLogger, Pump, Valve)				
• Ct Chargetek 500 Battery Charger				
• Cleaning Solutions				
• Extension Tubing For Sample Line From Funnel				
• Sample Bags (Alltech # 41012)				
<b>UltraSeep</b>				
• Meter (with Charged Battery)				
• Lift Bridle				
• Wheels and Pins				
• Cover for MiniLogger Display				
• MinLogger Display Cover in Place				
• Dummy Plug for MiniLogger RS-232 BC Connector				
• Misc Dummy Plugs				
<b>Computer and Cables</b>				
• Computer(S), UltraSeep Programs, Power Cords				
• ESM-1 Power/Com Interface Box				
• 100' ESM-1 Com Cable				
• 100' Cable for MiniLogger with Dummies				
• RS-232 Adaptor Cable with DB-9				
• External Switch for Pump to Put into Ext RS-232				
• 2 X 12-V Small Batteries to Power Solenoid Valve				
• GPS				
<b>Deployment/Retrieval</b>				
• Primer Bulb				
• Marker Buoy				
• Tie Wraps				
• Lift Bags				
• Ice Chest for Samples				

## APPENDIX D: UltraSeep Pre-Deployment Checklist

Refer to "Checklist For UltraSeep" for Necessary Items				
Battery Charged (Check Voltage?)				
Pump Tubing Loaded in Pump Head				
Intake Sample Line Attached at Funnel				
Sample Lines Attached to Bags				
Valve Stems on Bags Open (Pulled Out)				
Pouches Zip-Tied to Top to Retain Bags				
MiniLogger Programmed				
ESM-1 Programmed with Proper Delay and Valve Periods				
Start and Sample Sequence Start/End Noted in Log				
Release Shackle Attached to Bridle				
Wheels Removed				
Remove Air Bubbles Trapped in Funnel				
Prime Flow Tube				
Use Caution Not to Get New Air Bubbles Inside Funnel				
Zero Flow Tube				
Connectors/Cables Dummy Plugged				

## APPENDIX E: UltraSeep Cleaning Procedures

### CLEANING SCHEDULE (per line)

- 4 minutes detergent (2% Alconox<sup>®</sup> or RBS)
  - 2 minutes 10% acid (if necessary)
  - 2 minutes 18 mega-ohm deionized (DI) water
- 1) Prepare cleaning solutions in carbuoys:
    - a. 10 liters of 18 mega-ohm deionized water
    - b. 5 liters of warm 2% RBS or Alconox<sup>®</sup>, depending on analysis
    - c. 1.5 liters of 10% nitric acid if analyzing metals
  - 2) Attach the extension tubing to the detached sample line from the funnel. Place this line in the detergent container. Place a cup under each sample on the UltraSeep as fluids will drip from lines.
  - 3) Make sure tubing is loaded in the UltraSeep's peristaltic pump head. Power-up UltraSeep and connect computer to ESM-1 using interface box as described in "Communicating with Meter." Select "Shortcut to ESM" and upload "Clean4.esm" (see Appendix E).
  - 4) Start "Clean4" and inspect lines to make sure fluid is flowing. If there are flow problems, try raising the container to reduce the head.
  - 5) Have the acid and DI containers together for the next portion of the cleaning process as the intake line from the acid container will be switched halfway through the 4-minute cycle to the DI container for each sample line. The use of a stopwatch is recommended.
  - 6) Load the Teflon<sup>®</sup> sample bags into the mesh pouches with the valve stems pointing inward, through the mesh, and push onto sample tubing. Pushing the valve stem onto the tubing will close the valve stem. **It is necessary to pull the valve stem out to collect samples.**

## APPENDIX F: MiniLogger Set-Up

Note: The following should be done before programming the ESM-1

Select Shortcut to "Flowm" from computer desktop				
Connect MiniLogger com cable and RS-232 cable to computer RS-232				
Hit Enter to get prompt (takes a while or hit again)				
Type in "menu" (repeat typing in "menu" if you do not get it the first time)				
Go to METER FACILITIES (right arrow to select)				
Scroll to datalogger control (use up/down arrows then right arrow)				
Select "CLEAR DATALOGGER" > YES				
Go back to main menu (use left arrow)				
Select 2 CHANNEL FLOW using right arrow				
Select CHANNEL 1 FLOW TUBE				
Select Datalogger setup				
Select Datalogger mode				
Select "Yes" for MEMORY				
Once deployed, zero meter and save value as new zero value				

## APPENDIX G: ESM-1 Programming Highlights

Two programs are used for the programming of the ESM-1 controller/logger. A context editor is needed to write/change the programming scripts for the ESM-1; we use ConText Editor. The other program is Hyperlink, which communicates with the ESM-1.

The following are major areas for attention (also see following page):

### Context Editor

#### Edit "Main" File:

- Check the number of "repeats" for the startup delay and change to anticipate delay from the time of downloading program to ESM-1 to the time it begins sampling. Each repeat = **5 minutes**, ex. 36 repeats = 3 hours (default).
- Change filename for new site in two places.

#### Main Loop:

- Change the pump loop filename in 6 places at end of sub routine.

#### Edit "Pump" file:

- Outside repeat is the time between switching valves. One repeat = **10 minutes**, ex. 15 repeats = 2 ½ hours. Change, if necessary.
- Change filename for new site.

### ESM-1 Uploads

- Connect ESM interface box to computer and ESM
- "Shortcut to ESM", hit enter, wait for prompt, and type in "cd /store/eep/micro" to go to program area of ESM-1
- Type "dir" at new prompt to see list of programs on ESM
- Type "del 'filename'" to get rid of files if more memory needs to be cleared on the ESM for the new site (need 5000 bytes free for one tidal cycle at 5-minute sampling)
- Type "upload 'filename'" for pump file at prompt (name you want it to be called) and hit Enter. Should say "Ready to receive text"
- Go to Transfer menu, click "send text file"
- Select file to upload from C:\ESM (look at all file types) and open template file to upload to ESM-1. Inspect file while uploading to see if everything looks good.
- Hit Cntrl-C when done.
- Repeat from step "5" for uploading new "main" file.
- To run ESM, type in filename for "main" and hit enter.

### EDITING ESM-1 PROGRAM FILES

The following is a portion of the "main" file for programming the ESM-1. Nine places require attention:

#### Legend:

- repeat: used to delay water sampling sequence. Repeat = 5 minutes for "main" file, 10 minutes for "dump" file.
- site name: change in eight places and "save as" new file.

```
#start up delay
repeat 36 #***
  transmit 1,"Startup delay\r\n"
  burst 1000,300,"Flow","/store/cf/pw3a",display #***
end
```

```
#now start doing something real
execute "/store/eep/micro/pw3apump" #***
```

```
digitalio 10,set
wait 10000
transmit 3,"go2\r"
wait 5000
digitalio 10,clear
transmit 1,"go2\r\n"
execute "/store/eep/micro/pw3apump" #***
```

```
digitalio 10,set
wait 10000
transmit 3,"go3\r"
wait 5000
digitalio 10,clear
transmit 1,"go3\r\n"
execute "/store/eep/micro/pw3apump" #***
```

The following is a portion of the "pump" file with areas of attention highlighted:

```
#start pump loop
repeat 15 #number of times to repeat sample burst for each valve ***
  burst 1000,300,"Flow","/store/cf/pw3a",display #***
  flow02=[Analog 2]
  if flow02 > 23300 #4V ***
    transmit 2,"bm%100\r" #***
    transmit 1,"bm%100\r"
    wait 100
    transmit 2,"bmr\r"
```



## **APPENDIX H: UltraSeep Data Downloading**

### **Downloading data from the ESM-1**

- Hook up com cables
- "Shortcut to ESM" and hit Enter to get prompt
- Type in "cd cf" to change the directory to Compact Flash (ESM-1 memory) to see if filename setup during programming is listed.
- Type "extract /store/cf/'filename', synopsis, compact" but DO NOT HIT ENTER
- Go to "Transfer Menu">"Capture Text"> rename if you want new name.
- Hit Start then Enter
- Go back to "Transfer" menu > "Capture Text" > Stop

### **Downloading data from MiniLogger**

- FLOWM shortcut
- Type "logger" at prompt, but DO NOT HIT RETURN
- Go to "Transfer" > "Capture Text" > type in filename for site
- Click "Start" > Enter
- When data stream has stopped, go back to "Transfer Menu" > "Capture Data" > "Stop"

### **"Open Pipe"**

- Run ESM Shortcut
- Type "cd eep/micro" at prompt <enter>
- Type "initserial 3,9600" to initialize port 3 (valve port on ESM ) <enter>
- Type "digitalio10, set" to turn on converter ("digitalio10,clear" to turn off converter) <enter>
- Type "openpipe3" <enter>
- Type "go\_", use 1 through 6 in the blank to advance valve to position <enter>
- Type "cp" to ask where the valve position is presently located <enter>

## APPENDIX I: ESM-1 DATA PLOTTING

### Quick Check

In Microsoft® Excel, column A is flow, B is pressure (depth), and C is temperature.

- Open Microsoft® Excel
- Open file (look/find file in ESM folder where file is stored); it should appear as “(site name)syn\_compact.dat”
- Use “delimited” and “comma” when dialog box opens
- Highlight the particular column you want to graph (a, b, or c)
- Go to View > Insert Menu > Line graph

### Data Processing:

- Open the appropriate “.....syn\_compact.xls” and the “Seep meter Template.xls” files.
- Copy only the data values of A, B, and C columns of “.....syn\_compact.xls” file into the “raw data” sheet of the template file. Instructions are on the “raw data” sheet of the template and are as follows:

#### NOTES

1. Delete old data from yellow box (do not delete time column)
2. Paste new raw data (numbers only) into yellow box (from ESM syn\_compact.xls file)—use “paste as values” (clipboard icon with “12”)
3. Enter new start date/time in blue box (date/time for beginning of ESM file)
4. Enter in the row number for start time of sample #1 in the red box above
5. Make sure autofilter is turned off in Parse Data sheet
6. Delete old data from Parse Data sheet
7. Copy data from Raw Data sheet (including date/time)
8. Line up the first row of raw data at the line specified in red box above in the Parse Data sheet
9. Paste as values on the Parse Data sheet (clipboard icon with 12)
10. Put cursor at top of column one and autofilter data on Parse sheet for column one using a filter of 1 (use blue arrow at top of column one)
11. Delete raw data in purple box on the Formatted Data sheet
12. Copy the filtered data including time from the Parse data sheet (not including pump status)
13. Paste as values on the Formatted Data sheet (clipboard icon with 12)
14. Adjust plot ranges in plot sheets to match the length of the data in the Formatted Data sheet (in command line {fx})
15. Save the file under a new name that corresponds to the deployment name (Save As)

## APPENDIX J: MiniLogger Data Plotting

1. Import data file from logger in into Microsoft® Excel worksheet
2. Determine deployment start time-remove first 2 hours of data (adjustment period after deployment)
3. Check error codes, signal strength, and sound velocity ( $V_s$ ) in output file to assure proper operation of meter
4. Use average flow data to convert flow rate to specific discharge as follows:
  - a. Convert average flow rate to velocity by accounting for area of flow tube (area of flow tube = 0.7129 cm<sup>2</sup>)
  - b. Relate this velocity to velocity in funnel (ratio of funnel to flow tube is 0.0003411 for funnel area of 2090 cm<sup>2</sup>)
  - c. Convert from cm/sec to cm/day by multiplying by 86400 sec/day
  - d. Optional—convert to rate by adjusting for area of discharge for given time
5. Plot data—data usually plotted with tide